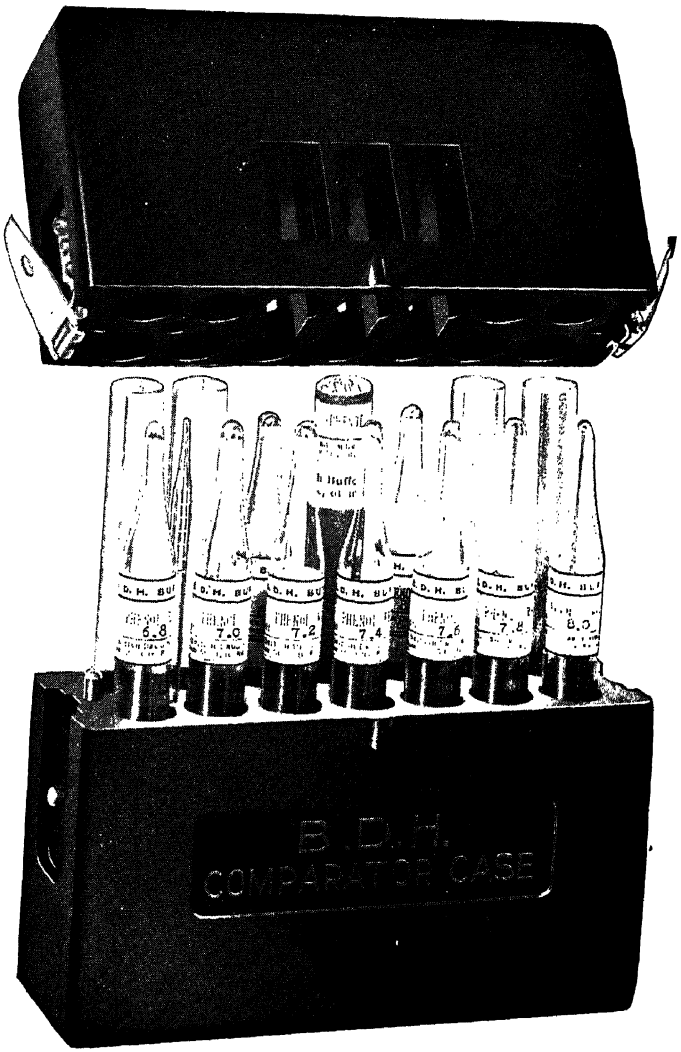
ELECTROCHEMISTRY

Volume I

BLACKIE & SON LIMITED
50 Old Bailey, LONDON
17 Stanhope Street, GLASGOW

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ELECTROCHEMISTRY

and

ELECTROCHEMICAL ANALYSIS

A Theoretical and Practical Treatise
for Students and Analysts

BY

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VOLUME I

ELECTROCHEMICAL THEORY

BLACKIE & SON LIMITED
LONDON AND GLASGOW

First published 1939

Printed in Great Britain by Blackie & Son, Ltd., Glasgow

PREFACE

It has been repeatedly suggested to me that I should write a practical guide to modern methods of Gravimetric Electrolytic Analysis. Except in a few instances these methods have hitherto found less application than might have been anticipated from their merits. Two reasons can be adduced for this. Firstly a certain mistrust exists in applying unfamiliar physical concepts to Chemical Analysis, and secondly it is commonly believed that the apparatus required is necessarily complicated and costly.

The first objection is in my view best met by a thorough discussion of principles. A detailed theoretical section was therefore written to form the first part of the book. It was realized later that this section might probably be found of interest to a wider circle, including students reading for pass and honours degrees. It has therefore been slightly expanded, and is now published separately as Volume I of the treatise. It will be seen that the exposition frequently deviates from that usually found in current text-books. Instances of this are the theory of the passage of the current through the interior of an electrolyte, the course of the neutralization of a weak acid by a strong base, the theory of the dependence of equilibrium potentials on activities, the Wien and the Dispersion effects, &c. In all deductions I have been at pains to make the treatment as direct and rigorous and at the same time as wide as possible.

In general, I have adopted the notation recommended by the Joint Committee of 1937 of the Chemical, Faraday, and Physical Societies. The abbreviations for references to scientific journals both in this and in subsequent sections of the treatise are those used by the Bureau of Chemical Abstracts.

It is hoped to publish shortly, as Vol. II, the sections dealing with Gravimetric Electrolytic Analysis and Electrolytic Marsh Tests. Relatively brief sections have also been included, dealing with Potentiometric and Conductimetric Titrations, Moisture Determination by means of Capacitance Measurement, and the Electrical Measurement of p_H, thus making the treatise cover the whole field of Electrochemical Analysis. In thus widening the field, I have been influenced by the fact that all branches of Electrochemical Analysis rely on the same theoretical principles, and can to a considerable extent be operated by the same apparatus. It is trusted that the treatise as a whole will thus contribute towards popularizing electrical methods and dispelling the belief that the apparatus need be a source of difficulty.

HENRY J. S. SAND.

LONDON, *July 1939*.

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Chapter I

ELECTROLYSIS. THE IONIC THEORY

When a difference of potential is applied to solutions of acids, bases or salts, or to certain substances in the molten condition, electrical conduction takes place, accompanied by changes of a chemical or physical nature. Such conduction is termed **electrolytic**, and the process, which is known as **electrolysis**, is distinguished by the fact that the products of the chemical change accompanying it appear separate from each other at the conducting plates, or " electrodes ", through which the current enters or leaves the liquid or " electrolyte ". It is further distinguished by being subject to Faraday's laws, which, condensed into a single statement, teach that the amount of chemical decomposition, expressed in gram equivalents, is proportional to the amount of current which has passed through the electrolyte. It is thus possible to define a number, which gives the amount of electricity that will liberate simultaneously one unit equivalent at each electrode, and is independent of the nature of the electrolyte. This number, known as **Faraday's constant**, or the **faraday**, and usually indicated by the symbol F, is equal to 96,500 coulombs per gram equivalent. Faraday's laws as originally propounded referred only to the products liberated at the electrodes. We shall, however, see later that they apply equally to the whole process of conduction through the electrolyte. Electrolytic conduction is further distinguished from metallic by the fact that specific conductance or **conductivity**, while varying from one electrolyte to another within wide limits, is of a smaller order than metallic conductivity. Thus the conductivity of the best conducting metal is about a millionfold that of the best conducting

electrolyte. Further, whereas the conductivity of metals and of alloys tends to decrease with rise of temperature, or to remain almost stationary, that of most electrolytes increases by about two or two and a half per cent per degree, approximately in inverse ratio to the viscosity of the liquid.

The electrode through which the positive current enters, or the negative current leaves the electrolyte, is known as the **anode,** that through which the negative current enters, or the positive current leaves the electrolyte, as the **cathode.** The terms " positive " and " negative " pole are ambiguous, the former term being usually applied to the electrode, through which the positive current leaves the electrolyte, in the case of a battery, but to the electrode through which it enters the electrolyte, in the case of a decomposition cell.

The Ionic Theory.

Adumbrated by Williamson in 1851, the ionic theory may be said to date from a paper by Clausius in 1857. Clausius pointed out that the validity of Ohm's law for electrolytic conduction required that free ions should exist in every electrolyte, independently of the applied difference of potential. In 1887 Arrhenius propounded the ionic theory independently, and in a series of brilliant investigations showed that quantitative conclusions drawn from it were in close agreement with experimental results. Almost universal acceptance was thus secured for it, and at the present day it may be said to form the foundation of all electrochemical theory.

According to the ionic theory the molecules of electrolytes are either partly or wholly broken up into charged part molecules, or **ions,** the charge on each gram equivalent being equal to Faraday's constant of 96,500 coulombs. Thus the molecules of dissolved sodium chloride consist largely of positively charged sodium **cations,** indicated originally by the symbol $Na^{\cdot}$, now usually by Na^{+}, and an equal number of negatively charged chlorine **anions,** indicated by Cl', or by Cl^{-}, whereas dissolved sodium sulphate similarly consists of sodium cations, and half their number of bivalent sulphate

anions, indicated by SO_4'', or by SO_4^{--}. The charge on 23 gm. of sodium ion is 96,500 coulombs of positive electricity, while 35·5 gm. of chlorine ion, or 48 gm. of sulphate ion, bear a similar negative charge. What was at one time probably the most serious difficulty presented by the ionic theory has been removed by modern theories of atomic structure. It was thought inconceivable, and contrary to chemical common sense, that, say, in a solution of sodium chloride free sodium and free chlorine should exist. According to modern views, however, a sodium ion is a sodium atom which has lost an electron, and the chlorine ion a chlorine atom, which has gained an electron, these changes in both cases making the respective ions chemically analogous to elements of the no-valency group, namely, to neon and argon respectively. Sodium ion and chlorine ion thus both become " chemically " inert, all their reactions being referable to their electric charges alone. In many cases an ion may combine by means of " covalencies " with other ions, or with the constituent atoms of molecules, thus building up a " complex " ion, which may bear either the same or a different charge from the original ion. Thus cobalt may form such ions as $[Co(NH_3)_6]^{+++}$, $[Co(NH_3)_5(H_2O)]^{+++}$, $ClCo(NH_3)_5]^{++}$, $[(CN)_6Co]^{---}$; and silver, an ion such as $[(CN)_2Ag]^-$. Complex ions may be present in solution in a state of chemical equilibrium with the simple ions from which they are derived, and the solution may or may not show the ordinary reactions of the latter, according to their concentration. In most cases, as we shall see, it is possible to calculate an equilibrium concentration of the simple ions from E.M.F. measurements, and to formulate intermediate reactions in which these ions take part. Thus it is possible to assume that the deposition of silver from a solution containing $[Ag(CN)_2]^-$ ions proceeds through the intermediate agency of Ag^+ ions, and even to calculate on the basis of this assumption how the equilibrium potential of the silver cathode should vary with $(CN)^-$ concentration. An agreement between the results of calculation and experiment, however, by no means proves that the mechanism assumed is correct. As a matter of fact, in

the case mentioned it has been shown that the calculated silver ion concentration is so minute that no question of the participation of silver ions in an electrode reaction can arise. Agreement between calculation and experiment in a case like this simply arises from the fact that calculations of the equilibrium conditions of a process are quite independent of the intermediate stages which have been assumed. This circumstance has often been overlooked.

It is quite probable that ions may be solvated, that is, joined by covalent bonds to the molecules of solvent, just as they are to extraneous molecules in complex ions. Thus the hydrogen ion is believed to consist mainly of the "hydroxonium" or "oxonium" ion $(H_3O)^+$, and only to a small extent, if at all, of the proton H^+. The fact that moving ions drag molecules of solvent with them by a process known as **electrophoresis** cannot be taken as evidence of solvation due to covalent bonds. Purely electrical forces would in any case cause them to pull the electrically unsymmetrical solvent molecules with them.

Deductions from the Ionic Theory. Ionic Equations.

Deductions from the ionic theory are mainly of two kinds. First we have those which are derived from the thermodynamical consideration of equilibrium conditions. These are based on the calculation of the **maximum work** obtainable from the transference of solute from a more to a less concentrated solution. For dilute solutions of non-electrolytes this work, sometimes called **osmotic work** is $(RT/C)dC$ per mol, if C represents the (practically equal) concentrations of the two solutions and dC their difference, and R and T have their usual significance. Where ionized particles are concerned, the work obtainable is smaller, for there is an electrical hindrance to the transference. The older theories ignore this electrical effect, and consequently the results are not correct except for extremely feeble ionic concentrations. However, all the pioneering work of Arrhenius, Ostwald, Van't Hoff, and others does not take the electrical effect into consideration, and we shall also in the meantime ignore it.

The concept of **activity**, introduced by G. N. Lewis for the purpose of meeting the difficulties of a more complete theory, we shall refer to later.

We may arrange our thermodynamical deductions in three main classes. First we have the consequences of " colligative " relations,* from which molecular concentrations and therefore apparent molecular weights may be derived. Examples of colligative properties are depression of freezing-point, elevation of boiling-point, osmotic pressure, &c. Secondly, there is the law of **mass action**, and thirdly, the deduction of **electrode potentials**, and potential differences generally.

Another class of deduction based on the ionic theory is the interpretation of the conduction of the current through the interior of a solution. Here the older and the more modern theories alike recognize that such conduction is due to the movement in opposite directions of cations and anions through the solution. Whereas, however, the older theories assume that under given electrical conditions the number of ions crossing any section of the electrolyte per unit time is simply proportional to their concentration, the modern theories recognize that in the more concentrated solutions there is a hindrance due to the non-random distribution of the ions, which is caused by their electric charges. Thus the " ion-atmosphere effect " is brought about. In addition to this there is a hindrance, which results from a motion of the solvent due to the ion-atmosphere, and takes place in opposition to the ion. This is known as the " electrophoretic effect ". These matters are discussed in Chap. V.

We now come to the considerations, on which one of the methods for the calculation of the **degree of dissociation** of an electrolyte is based. From the experimentally known concentration of the solution, c in grams per unit volume, we may calculate the **original molecular concentration** $C = c/M$, where M is the molecular weight of the non-

* A colligative property according to Ostwald is one which depends only on the molecular concentration of the solute (i.e. mols per unit volume), but not on any of its other specific properties.

ionized solute. Now let α be the fraction of the molecules which are ionized—usually termed " the degree of dissociation "—and let n be the number of ions resulting from the break-up of one molecule. Then the number of un-ionized mols per unit volume is $C - \alpha C$, the number of mols of ionic individuals is $n\alpha C$, hence the total number of mols (molecular and ionic) is $C - \alpha C + n\alpha C$, or $C[1 + \alpha(n - 1)]$. The ratio of this to the original molecular concentration C is usually designated by i, and termed *Van't Hoff's factor*. Thus

$$i = 1 + \alpha(n - 1). \quad . \quad . \quad . \quad . \quad . \quad (1)$$

On the basis of its definition Van't Hoff's factor may be determined as the ratio between depression of freezing-point experimentally determined and depression calculated from the " original " concentration of the solution. Any colligative property may be employed similarly for calculating i. From equation (1) α may then be derived. We shall consider later the wholly independent derivation of α from conductivity measurements.

Both classes of determination lead to the result that the solutions of strong acids, strong bases, and most salts are strongly ionized. Such electrolytes are termed **strong electrolytes.** In the case of binary strong electrolytes such as hydrochloric acid or sodium chloride almost complete dissociation, i.e. a value of $i = 2$, and $\alpha = 1$, is attained at great dilution, whereas with ternary electrolytes such as sulphuric acid, some approach to $i = 3$, $\alpha = 1$ is found. On the other hand, the solutions of weak acids and weak bases, such as acetic acid and ammonia, show only very slight deviations of i from 1, and are termed **weak** or **feeble electrolytes.**

It is generally assumed that chemical reactions between electrolytes take place by the intervention of their ions, and this has led to the use of ionic equations. These are derived by replacing molecules by the ions into which they dissociate, in the case of strong electrolytes, while in the case of weak electrolytes the molecules are written as such. Those ions which are left unchanged in a reaction are omitted. In ionic

equations obviously not only the atomic species but also the electric charges must balance, although the sum of the latter on each side of the equation need by no means be zero, as is exemplified by the chemical equations (*C*4) and (*C*5), p. 8. Thus entirely new interpretations have been placed on chemical reactions of electrolytes. The specific reactions of acids have been referred to the **hydrogen ion** or **hydrion** H^+, those of bases to the **hydroxyl ion** OH^-. The action of a strong acid on the salt of a weak one has assumed a new aspect. Before the advent of the ionic theory the acidic radical of the stronger acid was considered to seize the metal atom in the salt of the weaker one, leaving its hydrogen atom to combine with the weaker acid radical. According to the ionic theory, however, it is the anion of the weaker acid that seizes the free hydrogen ion of the strong acid to form undissociated weak acid. Representing the molecules of the strong and weak acid respectively by HA_s and HA_w, the salts by BA_s and BA_w, the older chemical equation

$$HA_s + BA_w = HA_w + BA_s$$

becomes in terms of the ionic theory on the principles just explained

$$H^+ + A_w^- = HA_w. \quad . \quad . \quad . \quad . \quad (C1)$$

Similarly, when the strong base B_sOH acts on the salt AB_w of the feeble base B_wOH, the result is represented by

$$OH^- + B_w^+ = B_wOH. \quad . \quad (C2)$$

The neutralization of an acid by a base, and the reverse process of hydrolysis, expressed according to the older views by the equation

$$HA + BOH \rightleftharpoons AB + H_2O,$$

are represented according to the ionic theory, (1) when both acid and base are strong, by the equation

$$H^+ + OH^- = H_2O; \quad (C3)$$

(2) when one of the two reactants is strong, and the other weak, by one of the two equations

$$HA_w + OH^- \rightleftharpoons A_w^- + H_2O \text{ (for a weak acid)}, \quad (C4)$$

or $$H^+ + B_wOH \rightleftharpoons B_w^+ + H_2O \text{ (for a weak base)}; \quad (C5)$$

(3) when both reactants are weak, by the equation

$$HA_w + B_wOH \rightleftharpoons A_w^- + B_w^+ + H_2O. \quad (C6)$$

The equation (*C*3), which represents a process proceeding practically to completion, and is independent of the particular acid and base employed, leads at once to the conclusion that the equivalent heats of neutralization of all strong acids by strong bases have the same value, a conclusion which is in agreement with experiment.

Chapter II

CONDUCTION OF THE CURRENT IN THE INTERIOR OF THE ELECTROLYTE

Transport Numbers.

The theory of the conduction of the current through the interior of the electrolyte was first given clearly by Kohlrausch in 1879. We imagine the portion of electrolyte considered to be of uniform cross-section, and a uniform potential gradient to have been established. The electrolyte contains cations and anions which, owing to their electric charges, will travel in opposite directions under the influence of a potential gradient, thus carrying current with them. This forms the complete explanation of the conduction of a current through an electrolyte. We imagine the electrolyte to be uniform in the part considered and imagine it cut by a plane on all points of which there is the same potential E.* Fig. 1 shows a section through this plane. To the right, at a distance dl, we imagine another plane, where the potential is $E + dE$, the gradient of potential in the slab of electrolyte between the two planes thus being $\frac{dE}{dl}$. Assuming this to be positive, cations will move from right to left, and anions in the opposite direction,

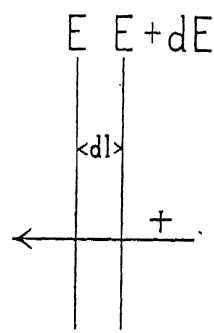


Fig. 1

* The limitations regarding uniformity of cross-section and concentration do not affect the conclusions to be arrived at. In a completely general deduction the plane surface would be replaced by an equipotential surface of any shape, and considerations would start from the flow of current across a small area δs during the small interval of time δt.

but not necessarily in equal quantities. Since we have postulated a stationary state, as much electricity will leave the slab of electrolyte per unit of time as enters it, and as the composition of the electrolyte to the left of the slab is the same as to the right of it, as much of each ion will likewise leave as enters it in any given time. We thus arrive at the conclusion that in the interior of a uniform electrolyte the passage of the current produces no change in composition. No such conclusion, however, is valid, if the electrolyte is not uniform. We imagine that the current has been passing for the time t, and indicate the gram equivalents of cations that have crossed our section from right to left (down the potential gradient) by K whether all of the same kind or not; the equivalents of anions that have crossed from left to right (up the potential gradient) by $\mathcal{A}$; the positive electricity that has been carried by the cations by $I_k t$, the negative electricity carried by the anions in the opposite direction by $I_a t$, the total amount of positive electricity that has passed from right to left by It, I therefore being the current strength. We thus have:

$$I_k t = FK, \quad I_a t = F\mathcal{A}, \quad . \quad . \quad . \quad (1a) \text{ and } (1b)$$

$$It = (I_k + I_a)t = F(K + \mathcal{A}), \quad (2a) \text{ and } (2b)$$

where F has its usual significance, viz. Faraday's constant, or the **faraday**, of 96,500 coulombs per gram equivalent.

We introduce here the concept of the **transport number** or **transference number**, of an ion in an electrolyte solution, and define it quite generally as the fraction of the current carried by the particular type of ion considered, across a section of the electrolyte such as that considered above and represented in fig. 1. Since the same amount of electricity is carried by the same number of g-equivalents of ions irrespective of their nature, we may also define the transport number as the ratio of the number of g-equivalents of the ion considered, which has crossed the section, to the total number which has crossed it in both directions. The latter number is the same as the number of g-equivalents liberated in a voltameter placed in series with the cell considered, and

can be readily determined. The definition of transport number here given by no means limits the number of types of ion to one cation and one anion, but if for our immediate purpose we do so, we may indicate the transport number of the cation by T_k, that of the anion by T_a; and the quantities K, $\mathcal{A}$, I_k and I_a introduced above will refer to only one type of ion. Indicating under these circumstances the transport number of the cation by T_k, that of the anion by T_a, we have by definition and by equations (1) and (2):

$$T_k = \frac{I_k}{I} = \frac{I_k}{I_k + I_a} = \frac{K}{K + \mathcal{A}}, \quad . \quad (3a)$$

$$T_a = \frac{I_a}{I} = \frac{I_a}{I_k + I_a} \quad \frac{\mathcal{A}}{K + \mathcal{A}}, \quad . \quad (3b)$$

and

$$T_k + T_a = 1. \quad . \quad (3c)$$

The Hittorf Method of determining Transport Numbers.

We now come to the description of the " Hittorf " electrolytic method of determining transport numbers. In doing so, we will drop the qualification that only one type of cation or of anion should be present. For our purpose we define the portion of electrolyte to the right of our section (fig. 1) as the anode chamber or compartment, that to the left as the cathode chamber or compartment, or, in general terms, the *anode chamber* is a part of the electrolyte which contains the anode, and is separated from the rest of the electrolyte by liquid of the original unchanged composition. The *cathode chamber* is defined in an analogous manner.

If the ion we are considering is a cation, it is travelling across our section (fig. 1) from anode to cathode compartment, and the number of g-equivalents which have travelled thus brings about an equal decrease in g-equivalents in the anode compartment, and also an equal increase in the cathode compartment. If the ion is an anion, the decrease is in the cathode compartment, and the increase in the anode com-

partment. Assigning now quite generally to the transport number of the ion considered the symbol T_k, if it is a cation, and the symbol T_a, if it is an anion, we have:

$$T_k = \frac{\text{decrease in anode chamber}}{\text{total equivalents travelled}}, \qquad (3d)$$

or

$$T_k = \frac{\text{increase in cathode chamber}}{\text{total equivalents travelled}}; \qquad (3e)$$

and

$$T_a = \frac{\text{decrease in cathode chamber}}{\text{total equivalents travelled}}, \qquad (3f)$$

or

$$T_a = \frac{\text{increase in anode chamber}}{\text{total equivalents travelled}}. \qquad (3g)$$

The quantities occurring in these equations may be derived from experiments, but their accurate meaning requires further explanation and some qualification. The words " decrease " and " increase " refer in the first instance only to amounts in g-equivalents of the ion considered. Further, they represent " gross " and not as a rule " net " values. In electrode chambers processes always take place at the electrodes, which consist either in the removal of ions from the liquid, or in the introduction of fresh ones into it. If these ions, as is often the case, are of the same kind as the ions considered, corresponding adjustments must be made.

As an example of the application of equations (3*d*) to (3*g*), we describe the experimental determination of the transport numbers of the Ag^+ and NO_3^- ion in silver nitrate by the Hittorf method. As we are in this case dealing with an electrolyte derived from only one cation and one anion, we can calculate the transport number of either from that of the other by means of equation (3*c*), viz. $T_{Ag} + T_{NO_3} = 1$. The experimental apparatus must comprise an electrolysis vessel in which the liquid around the cathode remains separate from that around the anode, and the intermediate electrolyte remains unchanged in composition during electrolysis. It is thus necessary after electrolysis, to separate the electrolyte

into a portion A, the anode compartment liquid, a portion B, which must be proved by analysis to have remained unchanged in composition, and a portion C, the cathode compartment liquid. The simplest type of apparatus to employ in the present instance is a straight glass tube of about 25 cm. length and 1·5 cm. bore, fitted at the bottom with a tap through which the anode, the intermediate, and the cathode liquid can be run in succession after the experiment. The cathode may be a silver or platinum disc placed near the top of the tube, the anode a spiral of pure silver wire placed at the bottom, the leading-in part of the latter being protected from contact with the liquid in the electrolysis vessel by means of a close-fitting glass tube. A current of about 10 milliamperes is passed through the apparatus for several hours. A copper voltameter is usually placed in series with the transport number apparatus, and from the increase in weight of its cathode the " total equivalents travelled " of equations (3*d*) to (3*g*) may be determined. In principle the same number could be obtained by measurement of the increase in weight of the cathode, or the decrease in weight of the anode in the electrolysis apparatus itself. Arrangements are sometimes also made for maintaining the current at a perfectly constant value I and measuring the duration in seconds t of the electrolysis. The total equivalents travelled may then be calculated by means of the expression It/F. After the electrolysis the liquid is run off in three successive portions A, B, C as already explained. We assume that analysis has proved the central portion B to have remained unchanged in composition, and the " net " increase in A and decrease in C to have been determined. Since the same amount of silver has dissolved from the anode as has deposited on the cathode, the increase in $AgNO_3$ in the anode compartment is exactly compensated by an equal decrease in the cathode compartment. It is thus only necessary to determine the increase in Ag^+ in the anode compartment, in order to find the other increases and decreases. To do this, the amount of anode liquid taken, and the original strength of the solution, must be known. The original amount of

silver in the anode liquid A can then be calculated, and the increase found by analysis.

We now come to the consideration of the relation which the experimentally determined " net increases " and " net decreases " bear to the " gross " increases and decreases of equations (3*d*) to (3*g*). We consider first the anion NO_3^-. As this is neither produced nor removed in the anode nor in the cathode compartment, we have a " net increase " in the former, and a " net decrease " in the latter, which is in each case identical with the corresponding quantity of equations (3*f*) and (3*g*). The analytically determined increase of equivalents of Ag in the anode compartment, which equals the increase of equivalents of NO_3, can therefore be directly utilized for determining T_{NO_3} according to equation (3*g*). As regards the cation Ag^+, however, the current is carried into the electrolyte at the anode by the formation of Ag^+ ions from metallic silver, and leaves at the cathode as a result of the removal of an equal amount of Ag^+ ions. For the calculation of T_{Ag} by equations (3*d*) and (3*e*) it would be necessary to find the gross decrease in the anode chamber by subtracting the measured net increase from the total equivalents travelled, and similarly the " gross increase in the cathode chamber " by subtracting the measured net decrease from the total equivalents travelled. An instance in which measured net decrease and increase in amount of cation would be employed without correction for the determination of T_k by means of equations (3*d*) and (3*e*) is furnished by a sodium hydroxide solution placed in a suitable transport number apparatus fitted with platinum electrodes.

There are some further considerations that must be applied to the determination of transport numbers. In precise experiments allowance is made for the solvent carried by the ions in their passage through the electrolyte. Such " electrophoresis " has already been referred to on p. 4. Obviously, if the positive ions carry the same amount of solvent as the negative, the result will be nil. If, however, different amounts are carried, there will be a resultant effect which may be described as an alteration in the concentration of the solvent.

According to a method due to Nernst, it can be measured by adding to the electrolyte a non-ionized substance, say boric acid or a suitable sugar, and measuring the change of concentration in this substance brought about by electrophoresis of the solvent during electrolysis.

There is yet another matter that must be discussed. The elements from which the ion under consideration is derived may also be present in other ions that are crossing the section represented by fig. 1. Thus, in a cadmium iodide solution, there will be Cd^{++} cations which pass from the anode to the cathode compartment. We know, however, for the reasons explained below, that at the same time the element cadmium is carried from the cathode to the anode compartment in the form of complex anions such as CdI_3^- or CdI_4^{--}. Thus, apart from any cadmium which may have been introduced by dissolution of a cadmium anode into the anode compartment, analysis of the contents of the latter shows an increase, and not a decrease, of the element cadmium with a correspondingly greater amount of iodine when concentrated solutions are employed. Such a result leads to a negative value of T_k and a value greater than 1 for T_a when equations (3*d*) and (3*g*) are employed for their calculation on the assumption that simple cadmium and iodine ions have carried the current. Since negative values and values greater than 1 for transport numbers are excluded by their definition, Hittorf was able to conclude from his experiments on concentrated cadmium iodide solutions that complex anions, such as those indicated above, exist in these solutions.

No general method is, however, known by means of which the share to be attributed to each type of ion can be determined. We must, therefore, accept all transport numbers with the proviso that they are based on the assumption of transference by a particular species of ion.

The fundamental theory of transport numbers is not affected by the presence of complex salts. Thus, if the electrolyte is potassium silver cyanide, the cation is K^+ and the anion $Ag(CN)_2^-$. The passage of the current therefore causes a gross increase of silver in the anode chamber, and a gross

decrease in the cathode chamber, which would lead to a negative value for T_k, if the current were wrongly assumed to be carried by silver ions.

The Moving Boundary Method of determining Transport Numbers.

We have seen that the electric current produces no change in the interior of a solution of uniform composition, but that changes are produced whenever the solution is not uniform. Sir Oliver Lodge showed in 1886 that when solutions containing different ions are brought into contact, and an electric current is passed through them, the motion of the ions can be made directly visible. Thus he connected two vessels containing dilute sulphuric acid by a bridge consisting of a glass tube filled with a gelatinized solution of sodium chloride. To this solution a little phenol-phthalein and sodium hydroxide had been added, thus giving it a crimson colour. An electric current passing through this combination caused hydrogen ions to enter the gelatinized solution and decolorize the phenol-phthalein. The motion along the tube of the boundary between colourless and crimson was observed, and from its velocity and the approximately known gradient of potential, a value for the velocity of the hydrogen ion under unit gradient of potential was calculated. At the present day gelatinized solutions are dispensed with, satisfactory methods for producing sharp boundaries between different solutions having been established and improved by Franklin and Cady in 1904, Denison and Steele in 1906, and MacInnes and his co-workers from 1923 onwards. (See *Chemical Reviews*, 1932, Vol. II, p. 171.) The theory of the moving boundary was developed by Kohlrausch in 1897, the conditions being laid down under which a boundary tends to become either sharper or more diffuse under the action of the current.

The method to determine the transport number of the cation K^+ in the salt KA as employed by MacInnes and his co-workers is explained by the diagram (fig. 2). Obviously it is equally applicable to the determination of the transport number of the anion A^-. An "indicator" solution is made

up containing the same anion A^- as the " test " solution, but a different cation K_1^+ indicator and test solution being of approximately equi-equivalent strength. The lighter of the two solutions is floated on the top of the heavier, so that a sharp boundary is obtained. This can be observed if there is a difference of refractive index. In fig. 2 the test is shown floated on the top of the indicator solution, and we shall assume it to have a smaller refractive index than the latter. In this case the boundary is illuminated from below by means of a narrow beam of light in such a manner that the beam is totally reflected from it, thus enabling its position to be accurately located by a suitable optical arrangement. This method for locating the boundary was first proposed by Abegg and Gauss in 1902, and improved by MacInnes and Cowperthwaite in 1929.

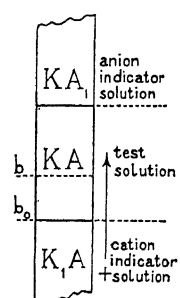


Fig. 2

It is essential that the " test " ion should be the " leading " ion, i.e. in the example illustrated by fig. 2, that the current should travel upwards. It is also necessary that the leading ion should have a greater velocity under the influence of a given potential gradient than the following one, in order that the boundary may remain sharp, and if it should have been disturbed, may recover. This may be understood as follows. Firstly, the solutions being of approximately equivalent strength, there will be a steeper potential gradient in the indicator solution containing the slower ion than in the test solution, and therefore if any of the test ion has found its way into the indicator solution, it will tend to overtake and come back to its fellows in the latter. Similarly, if any indicator ion finds its way into the test solution it will tend to fall back to its fellows. Apart from this, any test ion coming into the indicator solution will tend to overtake the indicator ions owing to its greater velocity under a given potential gradient, and thus to come back into the boundary, and similarly indicator ions that have strayed into the test solution will

tend to fall back into the boundary. The sharpness of the boundary having been assured, it will be understood why the test solution must be the leading solution, for only thus is it assured that the test ions travel throughout through solution of uniform composition which thus remains unchanged in concentration during an experiment. Assume, for example, that the boundary has travelled from b_0 to b, then the test ion has travelled throughout through solution of the original concentration C. If therefore during this journey the boundary has swept out the volume v, and if the concentration C is expressed in g-equivalents per unit volume, then the number of g-equivalents of K which have travelled is vC. The total number of g-equivalents which have travelled is also known, viz. It/F (p. 13). The transport number of the cation K is therefore

$$T_k = \frac{vCF}{It},$$

an expression which contains only quantities that can be readily determined.

Adhering to our example, we may find it convenient to float on the top of the test solution a third electrolyte containing the same cation K as the test solution, but a different anion A_1^- with a smaller velocity than A^-. Under these circumstances the boundary between A^- and A_1^- will travel downwards, and the ratio of its velocity of travel to that of the boundary between K^+ and K_1^+ will give us directly the ratio of the velocities of the ions A^- and K^+ under the same gradient of potential.

Ionic Mobilities and Velocities, Conductivity and Equivalent Conductivity. Arrhenius' Method for the Determination of α.

We now come to the more detailed study of the quantities K and A, p. 10, that is the gram equivalents of cation and anion, that have crossed our section of the electrolyte shown in fig. 1, p. 9, and the corresponding quantities I_k and I_a,

i.e. the current carried. The variables, on which the quantities considered depend, are the gradient of potential dE/dl, the area s of the section, the (equal) equivalent concentrations C_i of cations and anions, and the time t. The older theory assumes simple proportionality as the guiding principle. We indicate the proportionality factors of K and $\mathcal{A}$, i.e. the values, which these quantities assume, when all the variables are equal to unity, by u_k and u_a, and the corresponding proportionality factors of I_k and I_a by l_k and l_a. The constants u_k and u_a are termed the **velocities of the ions**, the constants l_k and l_a the equivalent ionic conductances or **mobilities.** We thus have:

$$K = u_k C_i s \frac{dE}{dl} t, \qquad \mathcal{A} = u_a C_i s \frac{dE}{dl} t, \quad . \quad (4a) \text{ and } (4b)$$

$$\frac{FK}{t} = I_k = l_k C_i s \frac{dE}{dl}, \qquad \frac{F\mathcal{A}}{t} = I_a = l_a C_i s \frac{dE}{dl}. \quad (5a) \text{ and } (5b)$$

These equations call for some remarks.

First the designation " velocity " for the constants u_k and u_a. If K_0 is the value of K, when s, dE/dl, and t are unity, then $u_k = \frac{K_0}{C_i}$. But $\frac{K_0}{C_i}$ is the volume of electrolyte, which contains K_0 gram equivalents of cation, or the length of a cylinder of unit cross-section, containing this amount of electrolyte. If therefore we imagine this cylinder with its K_0 gram equivalents of cations moving across unit section during unit time, it will have travelled the distance K_0/C_i or u_k. Hence u_k is the distance travelled by the cations under the influence of unit potential gradient, in unit time, or their velocity under the influence of unit potential gradient. It may be easily confirmed that the dimension of u_k is cm./sec. per volt/cm. in a cm.-sec.-volt system. The same considerations of course apply to u_a.

The proportionality postulated in our equations between the flow of ions and their concentration is based on the

assumption that the presence of charged ions does not interfere with the flow of their fellows. We have already seen (p. 5) that this assumption is now recognized as valid only for the most dilute solutions. Hence the conclusions drawn from our equations generally hold only for very low ionic concentrations.

The proportionality of the flow of ions to the potential gradient, on which the validity of Ohm's law for electrolytic conduction depends, holds in all cases of contemporary practical importance. However, where the potential gradients are so great as to affect ionic distribution in the electrolyte, this proportionality is now recognized to break down.

We come to the mathematical consequences of our fundamental equations. From equations (4) and (5) we find:

$$l_k = Fu_k \qquad l_a = Fu_a \qquad (6a) \text{ and } (6b)$$

and employing also equations (2), (4*a*), (4*b*),

$$I = F(u_k + u_a)C_i s\frac{dE}{dl} = (l_k + l_a)C_i s\frac{dE}{dl}. \qquad (7a) \text{ and } (7b)$$

We now introduce the concept of the **specific conductance** or **conductivity** κ of the electrolyte, which we may define as the value of I, when s and dE/dl are unity. Hence

$$\kappa = F(u_k + u_a)C_i = (l_k + l_a)C_i. \qquad (8a) \text{ and } (8b)$$

The conductivity is often, though somewhat redundantly referred to as the "specific conductivity". We further introduce the "original" equivalent concentration C of the solution, found by dividing the weight of electrolyte present per unit volume by its equivalent weight, its reciprocal v, the dilution $v = 1/C$, and the degree of dissociation α defined by

$$\alpha = \frac{C_i}{C}; \qquad (9)$$

also the **equivalent conductivity** Λ, defined by

$$\Lambda = \frac{\kappa}{\sim} = \kappa v. \qquad (10a)$$

The value of Λ at very low concentration (high dilution) we indicate by Λ_0 (frequently designated by Λ_∞) and term it the *equivalent conductivity at infinite dilution.* The corresponding very low concentration we denote by C_0 and the corresponding value of κ by κ_0. Then by (10*a*)

$$\Lambda_0 = \frac{\kappa_0}{\sim}. \qquad (10b)$$

Since theoretically at the very low concentration C_0, α approaches 1 therefore by equation (9) $C_i = C_0$ and hence by equation (8*b*)

$$l_k + l_a = \frac{\kappa_0}{C_0};$$

and using (10*b*) $\qquad \Lambda_0 = l_k + l_a, \qquad (11a)$

or, by (6), $\qquad \Lambda_0 = F(u_k + u_a), \qquad (11b)$

and, by (8*b*) and (11*a*), $\qquad \kappa = \Lambda_0 C_i. \qquad (12)$

Using (9), (10*a*) and (12), we have

$$\alpha = \frac{C_i}{\sim} = \frac{\Lambda}{\Lambda_0}. \qquad (13)$$

From equations (3*a*), (3*b*), (4), (5), and (11*a*) we find:

$$T_k = \frac{u_k}{u_k + u_a} = \frac{l_k}{\Lambda_0}, \qquad (14a)$$

$$T_a = \frac{u_a}{u_k + u_a} = \frac{l_a}{\Lambda_0}. \qquad (14b)$$

The equations we have deduced form the basis of the determination of highly important electrochemical constants, and of the theory of conductimetric analysis. We refer first

to equations (11*a*) and (11*b*). Equation (11*a*) may be expressed in words as follows:

The equivalent conductivity of an electrolyte at zero concentration (infinite dilution) equals the sum of the ionic mobilities.

This generalization, which constitutes an instance of the law, that the properties of electrolytes are additive, has been verified to a great degree of accuracy, and is known as *Kohlrausch's Law of the Independent Migration of Ions.* It was first enunciated in 1875.

The determination of individual ionic mobilities is thus a matter of importance. First Λ is determined from conductivity measurements on very dilute solutions of strong electrolytes, equation (10*a*) being utilized. It is necessary to confirm that the values obtained for Λ at sufficiently low concentration become almost independent of further dilution, so that Λ_0 may be found by extrapolation from finite values to zero value of C. It is impossible to obtain values for Λ_0 in this way for weak electrolytes, since secondary influences would interfere at the extreme dilutions which would be necessary. The transport numbers of the ions of the strong electrolyte chosen must next be determined at sufficiently low concentration, and by making use of equations (14) and (6), it is then possible to determine individual ionic mobilities and velocities. The mobility of one type of ion having been obtained, it is possible to determine that of another, by finding the equivalent conductivity at infinite dilution of a strong electrolyte that contains them both, and then making use of Kohlrausch's law. Thus it is possible to construct a complete table of the mobilities of all the more important ions. A table of mobilities is given in the section on conductivity titrations (Vol. III). The units in which mobilities and equivalent conductivities are expressed have the dimension $\text{cm.}^2/\text{ohm} \times g\text{-equivalent}$. Conductivities are stated in the unit $1/\text{ohm} \times \text{cm.}$ (or amp./volt $\times$ cm.), known as the Mho, or else in a unit one-millionth of this, known as the gemmho. Frequently the mho is also defined as a unit of conductance having the dimension 1/ohm. In order to find equivalent conductivities, it is thus necessary to divide the

conductivities, measured in mhos by the concentration measured in *g*-equivalents per cm.^{3}. "Mobilities" of ions have also been calculated, starting from conductivities at finite instead of infinitely small concentrations.

Kohlrausch's law makes it possible to determine Λ_0 for weak electrolytes. In the case of a weak organic acid, for example, it is possible to determine Λ_0 for the sodium salt (usually from experiments on dilute solutions in the presence of excess weak acid to minimize hydrolysis). By adding to this the known difference between the mobilities of the hydrogen and the sodium ion, Λ_0 for the weak acid is then found. After this it is possible to find α by utilizing equations (10*a*) and (13). This is the **Arrhenius method,** which is more accurate than that based on the measurement of freezing-point depressions or similar colligative properties (p. 6). There is a general, though by no means an accurate, agreement between the values of α determined from conductivities and from colligative properties (*vide* Chap. V).

For remarks on the definitions employed in the preceding chapter the reader is referred to the addenda on page 128.

Chapter III

APPLICATIONS OF THE LAW OF MASS ACTION TO THE IONIC THEORY

Ionic equilibria have been tested extensively by the application of the law of mass action. A very considerable amount of agreement is found between the results of theory and experiment for low ionic concentrations, and this has contributed greatly to the general acceptance of the theory. For high ionic concentrations the theoretical results are completely at variance with experimental fact. The reasons have already been briefly pointed out. The disagreement is usually referred to as "*the anomaly of strong electrolytes*".

Deductions from the law of mass action hold rigidly, when "activities" are substituted for concentrations, and so-called equilibrium constants become rigorously constant, when such substitution has been carried out. As explained in Chap. V, activities are thermodynamically corrected concentrations, the correction being usually effected by means of a factor known as the *activity coefficient*. Equilibrium constants corrected by means of activity coefficients are known as *true* or *thermodynamical* equilibrium constants. Inversely, from true equilibrium constants, such as *true ionization constants*, activities may be derived. Molecular concentrations (usually in mols per litre) of a species are indicated by enclosing the chemical formula of the species in a bracket such as is exemplified by the symbol $[H_2O]$ or $[H^+]$, whereas activities are expressed by brackets exemplified by $\{H^+\}$. Since activity coefficients are relatively seldom known, we shall in the present book generally draw no distinction between concentrations and activities, and only on occasion use the symbol

for activities in expressions which lend themselves to the calculation of activities.

The Ostwald-Planck Dilution Law.

The Ostwald-Planck dilution law is the equation expressing the variation of degree of dissociation with concentration or dilution for binary electrolytes. Its application is confined to univalent molecules. We have thus to consider mainly the two cases:

$$HA_w = H^+ + A_w^-, \quad . \quad . \quad . \quad . \quad (C7a)$$

and

$$BOH = B^+ + OH^-, \quad . \quad . \quad . \quad . \quad (C7b)$$

in which HA_w and BOH are the molecules of the undissociated weak acid or base, and the other symbols have their usual significance. We indicate the " original " molecular or equivalent concentration of the electrolyte * by C, the dilution $1/C$ by v, and the degree of dissociation by α. Then the concentration of the undissociated molecules is $C - \alpha C$, and that of each ionic species αC. The application of the law of mass action leads after slight simplification to the equations

$$K = C\frac{\quad}{1-\alpha} - \frac{\quad}{v(1-\alpha)}, \quad (1a) \text{ and } (1b)$$

in which K is the so-called **dissociation** or **ionization constant** of the electrolyte. This formula shows good agreement with experiment for weak univalent acids and bases, and also for such bivalent weak organic acids as succinic acid, which dissociate in successive stages, yielding in the first instance a univalent anion derived from the undissociated molecule by the loss of only one hydrogen ion. In most cases α is so small that we may replace $1 - \alpha$ by 1, thus simplifying equation (1a) to

$$\alpha = \frac{\sqrt{K}}{\sqrt{C}}. \quad (1c)$$

* i.e. concentration calculated as on p. 20 on the assumption that there is no dissociation, i.e. mass of solute per unit volume divided by molecular or equivalent weight.

It will be noticed that the dimension of the dissociation constant is that of a concentration. A simple definition based on this fact follows from the discussion of indicators and of the neutralization of weak acids (p. 46). The unit usually employed is the mol per litre, but a unit one-hundredth of this, and also the mol per c.c., are met with. It will be seen that the common practice of omitting to state the dimension of units cannot be defended.

It is only when dissociation constants are small that the Ostwald-Planck dilution law holds. Thus for acetic acid K is about one fifty-thousandth molar.

Dissociation constants of weak acids and bases are of great importance. They may be readily determined for such acids or bases as acetic acid or ammonium hydroxide by means of equations (1*a*) or (1*b*), α being found from conductivity measurements as described in Chap. II. For extremely weak acids or bases recourse must be made to measurements of hydrogen ion concentration, as indicated on p. 46, and discussed more fully in Book III.

It has been found in recent times to be convenient to extend a practice introduced by Sørensen in 1909 for indicating small hydrion concentrations, to other concentrations and their functions. Sørensen suggested the introduction of the function p_{H} (hydrogen ion exponent or power), defined by the equation

$$p_{\mathrm{H}} = -\log_{10} [\mathrm{H}^+], \qquad (2)$$

where $[\mathrm{H}^+]$ is the hydrogen ion concentration expressed in gram ions per litre. Another way of expressing Sørensen's suggestion is:

$$[\mathrm{H}^+] = \left(\frac{1}{10}\right)^{p_{\mathrm{H}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

The practice may be extended by defining generally the function p_K of a concentration or of a product of concentrations K by the equation

$$p_{\mathrm{K}} = -\log_{10} K. \qquad (3)$$

Herein K may therefore be the dissociation constant of an acid expressed in mols per litre. We may call p_K the K exponent. It should be noted that although the definition of p_H just given is the original one, yet it is being gradually displaced by one in which $[H^+]$ means the *activity* of the hydrogen ions, and that the standard potentiometric method of estimating p_H gives its value in terms of activity and not of concentration. Similarly p_K is best defined by assigning to K the meaning of the *thermodynamical equilibrium* or *ionization constant.*

The Solubility Product.

The theory of the solubility product deals with the effect of adding to the saturated solution of a sparingly soluble highly ionized salt a readily soluble salt having an ion in common with it. Let the sparingly soluble salt have the chemical formula B_bA_a, dissociating according to the equation: $B_bA_a \rightleftharpoons bB^+ + aA^-$, and to fix our ideas let interest attach to the solubility of the basic ion B^+. The salt is supposed to be so highly ionized that the amount of B in the undissociated portion is negligible compared with the amount present as ion, and that the solubility may thus be taken as equal to the concentration of the B^+ ion. A readily soluble salt having the A^- ion in common with the given salt is added, thus bringing the concentration of A^- to the value $[A^-]$. The problem is to find the concentration $[B^+]$ of the ion B^+. The solubility $[B_bA_a]$ of the undissociated portion is supposed to be unaffected by the presence of other molecular species. Since B_bA_a is in equilibrium with its ions, we have, by the law of mass action,

$$[A^-]^a\,[B^+]^b = K[B_bA_a] = \text{constant} = K_s, \quad . \quad (4)$$

or, for a binary electrolyte,

$$[A^-]\,[B^+] = K_s. \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

The constant K_s is known as the **solubility product.** As already explained, it is often convenient to introduce a new

constant p_s, called the *solubility exponent*, which is defined by

$$p_s = -\log_{10} K_s, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

the concentrations constituting K_s being measured in mols per litre.

As an instance to which the theory may be applied, we imagine a solution of potassium chloride in contact with solid mercurous chloride, and inquire how the solubility of the mercurous ion varies with the concentration of the chloride ion. To have a numerical example we compare the solubility of the mercurous ion when the potassium chloride is tenth normal with that when it is normal, assuming the chloride ion concentration to be ten times as great in the latter as in the former case. The mercurous ion is known to exist mainly in the form of a bivalent ion having the formula Hg_2, so that we have the equilibrium: $Hg_2Cl_2 \rightleftharpoons Hg_2^{++} + 2Cl^-$; and hence

$$K_s = [Hg_2^{++}]\,[Cl^-]^2.$$

Distinguishing concentrations when the potassium chloride is tenth normal from those when it is normal by the indices A and B, we thus have

$$K_s = [Hg_2^{++}]_A\,[Cl^-]_A^2 = [Hg_2^{++}]_B\,[Cl^-]_B^2$$

or

$$[Hg_2^{++}]_A : [Hg_2^{++}]_B = [Cl^-]_B^2 : [Cl^-]_A^2 = 100.$$

We therefore see that in the tenth normal solution the concentration of the mercurous ions is a hundredfold that which it is in the normal solution of potassium chloride. We shall have occasion to employ this result in connexion with the theory of the calomel electrode. For the determination of the solubility product of AgCl see p. 89.

Other Ionic Concentration Products.

A relation very similar to the one just considered is that between the concentration of one of the ions of a weak acid or base and that of the other ion.

Take, for example, an N/100 solution of acetic acid, in which the degree of dissociation is slightly over 4 per cent, and the hydrion and acet-ion concentrations therefore about 4×10^{-4} normal, and compare this with a solution of the same original acetic acid concentration, in which, however, the concentration of the acetic ions has been made N/10 by the addition of sodium acetate in suitable concentration. Using the same notation as previously, we have

$$\frac{[H^+]\,[A^-]}{[HA]} = K'.$$

Now, in the case considered the concentration of the undissociated acid differs from the "original" concentration, which we may indicate by $[HA]_0$ by only 4 per cent, and we may therefore for our present purposes replace [HA] by $[HA]_0$, obtaining the relation

$$[H^+]\,[A^-] = [HA]_0 K' = \text{constant} = K.$$

Distinguishing ionic concentrations in the absence and presence of added sodium acetate by the indices A and B, we have therefore

$$K = [H^+]_A\,[A^-]_A = [H^+]_B\,[A^-]_B,$$

or

$$[H^+]_B : [H^+]_A = [A^-]_A : [A^-]_B = 4 \times 10^{-4} : 10^{-1} = 1/250;$$

or in words: The addition of sodium acetate in the quantity mentioned has the effect of reducing the hydrion concentration to one two-hundred-and-fiftieth part of its value, or in increasing the p_H of the solution by log 250 = 2·40.

In a similar way the presence of hydrochloric or other strong acid in a N/100 acetic acid solution in such quantity as to make the hydrion concentration tenth normal will reduce the acetic ion concentration to one two-hundred-and-fiftieth of its value, thus diminishing the degree of dissociation from about 4 per cent to negligible proportions.

Similar considerations regarding the effect of salts and of

strong bases apply to the dissociation of weak bases. On the other hand, when to solutions of strong acids or bases their salts are added, results which have been termed *the neutral salt effect* are obtained. These are completely at variance with the theory we have given, the apparent hydrion concentration being sometimes increased instead of decreased.

The Ionic Product of Water.

Even the most carefully purified water shows a certain conductivity, which is ascribed to the presence of hydrogen and hydroxyl ions. This conductivity is, according to equation 8*b*, Chapter II (p. 20), expressed by the equation

$$\kappa = C_i(l_{\mathrm{H}} + l_{\mathrm{OH}}),$$

from which C_i, the equal concentration of the hydrogen and hydroxyl ions, may be calculated. According to Kohlrausch and Heydweiller's determinations in 1894, the value of C_i at 18° C. is $0{\cdot}8 \times 10^{-7}$ *g*-equivalents per litre. In all aqueous solutions the hydrogen and hydroxyl ions are in equilibrium with undissociated water. Therefore, indicating as before concentrations by square brackets, we have

$$K' = \frac{[\mathrm{H^+}]\,[\mathrm{OH^-}]}{[\mathrm{H_2O}]}.$$

The concentration of the undissociated water molecules in all aqueous solutions up to, say, normal strength may be taken as constant, viz. about 1000/18 mols per litre. For all such solutions we may therefore write

$$[\mathrm{H^+}]\,[\mathrm{OH^-}] = K'\,[\mathrm{H_2O}] = \text{constant} = K_w. \quad . \quad (6)$$

Here again it is useful to introduce the new constant p_w, defined by

$$p_w = -\log K_w, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where K_w is expressed in (*g*-equivalents per litre)^2.

The numerical value of K_w at 18° is calculated from Kohlrausch and Heydweiller's value of C_i to be $(0{\cdot}8 \times 10^{-7})^2 = 0{\cdot}6 \times 10^{-14}$ (*g*-equiv. per litre)^2. This value increases rapidly

with temperature, rising to over 10^{-14} at 25°. For most purposes it is sufficient to assume $K_w = 10^{-14}$, hence $p_w = 14$. We may thus write for all aqueous solutions:

$$[H^+]\,[OH^-] = 10^{-14}, \quad . \quad . \quad . \quad . \quad (7a)$$

or

$$p_H + p_{OH} = 14. \quad (8)$$

The following examples of p_H values may be given. Following from the definition, equation (2), p. 26, we have, in a normal solution of hydrogen ions, $p_H = 0$, in a tenth normal solution $p_H = 1$, in a hundredth normal solution $p_H = 2$, &c.; on the other hand, following from equation (8), in a normal solution of hydroxyl ions the approximate value is $p_H = 14$, in a tenth normal solution $p_H = 13$, in a hundredth normal solution $p_H = 12$, &c. The p_H in a neutral solution, in which $[H^+] = [OH^-]$, is $p_H = 7$.

The ionic product of water K_w has also been determined by a number of methods not directly connected with conductivity measurements. Of these, the method based on the determination of the hydrolysis of salts is explained on p. 33, and that based on E.M.F. measurements on p. 88. Other methods exist, the discussion of which would lead us beyond the main subject of this book. All the results are in sufficient agreement with those obtained from conductivity determinations, and this furnishes a powerful argument in favour of the correctness of the assumptions on which the theory is based.

Hydrolysis.

The amphoteric character of water, i.e. its behaviour both as a weak acid and a weak base, is governed by the hydrogen and hydroxyl ion concentration as expressed by equation (6), and is the cause of the hydrolytic dissociation or hydrolysis of salts. The theory of this phenomenon is of great importance in various branches of electrochemical analysis.

Salts derived from one Weak and one Strong Component

We consider first the hydrolysis of a salt, in which only the acid constituent is weak. The corresponding case where only the basic constituent is weak is derivable from this by interchanging the acidic and basic and the hydrogen and hydroxyl ions. We confine ourselves to univalent binary salts.

We have seen that the neutralization of a weak acid by a strong base does not proceed to completion but is governed by the equilibrium equation (*C*4), p. 8. When the process related to this equation proceeds from right to left, we term it hydrolysis. Exchanging reactants and resultants in equation (*C*4), we write

$$A_w^- + H_2O \rightleftharpoons HA_w + OH^-. \quad . \quad . \quad (C4a)$$

We indicate the " original " (see p. 20) concentration of the salt A_wB by C, the fraction hydrolysed by x, and assume the concentration of ionized salt and of hydrogen ions to be negligible compared with the concentrations of the molecular and ionic species contained in equation (*C*4*a*), which as usual we indicate by square brackets. We thus have:

$$[A_w^-] = C(1 - x); \; [HA_w] = [OH^-] = Cx; \qquad (9a), (9b), (9c)$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{K_w}{Cx}. \qquad (9d), (9e)$$

Applying the law of mass action to the above equilibrium equation (*C*4*a*), we obtain, after simplifying,

$$\frac{Cx^2}{1 - x} = K'[H_2O] = \text{constant} = K_h. \quad . \quad . \quad (9)$$

The constant K_h, which we designate the **hydrolysis constant** of the salt, we may express in terms of the dissociation constant of the weak acid by applying the law of mass action to the equilibrium equation

$$HA_w \rightleftharpoons H^+ + A_w^-, \qquad (C7a)$$

and expressing the concentrations in terms of C and x. We thus find

$$K_a = \frac{K_w (1 - x)}{Cx^2},$$

and making use of equation (9) above and transposing,

$$K_h = \frac{K_w}{K_a}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

In most cases hydrolysis is small, so that $1 - x$ may be replaced by 1. Equation (9) then simplifies to

$$x = \frac{\sqrt{K_h}}{\sqrt{C}} = \frac{K_h'}{\sqrt{C}} = K_h' \sqrt{v}. \qquad (11a), (11b), (11c)$$

The degree of hydrolysis of a salt of the kind we are considering may be determined experimentally at varying concentrations by a number of methods. Thus $[OH^-] = Cx$ may be estimated by measuring the rate of saponification of esters placed in the solution of the salt, and K_h may be calculated at various concentrations according to equation (9). The validity of this equation may thus be tested.

Hydrolysis constants may also be calculated from equation (10). Alternatively this equation has been utilized for determining K_w when K_h was estimated independently. The values so obtained are in general agreement with that found from conductivity measurements (see p. 30).

The degree of hydrolysis may also be determined from measurements of colligative properties. From the chemical equation (*C4a*), p. 32, it will be seen that in a binary electrolyte the total molecular concentration of solute is increased by Cx as the result of hydrolysis. It thus becomes necessary to determine what would be the total molecular concentration in the absence of hydrolysis. This may be deduced from experiments in which a known excess of the acid HA_w is added, sufficient to make hydrolysis negligible.

For purposes of electrochemical analysis the most important aspects of hydrolysis are its effects upon the conductivity

and upon the p_H of the solution. Each of these effects may be used as a basis for quantitative determination.

Effect on Conductivity.

If the original concentration of the solution is C, then according to the chemical equation (*C4a*), Cx equivalents of A_w^- have been replaced by OH^-. If therefore the conductivity without hydrolysis would have had the value $\kappa' = C(l_{A_w} + l_B)$ the conductivity with hydrolysis is

$$\kappa = \kappa' + Cx(l_{OH} - l_{A_w}),$$

or

$$\frac{\kappa}{\kappa'} = 1 + x\,\frac{l_{OH} - l_{A_w}}{l_{A_w} + l_B}. \qquad . \quad . \quad (12)$$

The value of κ' can be found experimentally by adding a known excess of the weak acid HA_w. The correction to be made for the increase of hydrogen ion thus produced may be controlled by applying the law of mass action to equation (*C7a*), p. 25, in which $[HA_w]$ is made equal to the acid added per unit volume and $[A_w^-]$ equal to C. It will be seen that in the cases under consideration hydrolysis increases conductivity. Since l_{OH} is about three times as great as the mobility of most acidic or basic ions, and we may for purposes of rough approximation assume these equal, we may say that in many cases a percentage increase in conductivity is produced which is approximately equal to the percentage degree of hydrolysis. To obtain a correction for the hydrolysis of a salt derived from a weak base and a strong acid, we must replace l_{OH} by l_H, which is about five times as great as the mobility of most other ions, so that in this case a percentage increase in conductivity is produced which is often approximately twice the percentage degree of hydrolysis.

Effect on p_H.

For a salt derived from a weak acid and a strong base with slight hydrolysis we find, using equations (9*c*), (11*a*), and (10),

$$[OH^-] = Cx = \sqrt{CK_h} = \sqrt{C\frac{K_w}{K_a}},$$

and introducing logarithms and p_K values and making $\sqrt{K_w} = 10^{-7}$,

$$p_{OH} = 7 - \tfrac{1}{2}p_A - \tfrac{1}{2}\log C, \quad . \quad . \quad . \quad (13)$$

from which, using equation (8), we conclude that

$$p_H = 7 + \tfrac{1}{2}p_A + \tfrac{1}{2}\log C. \quad . \quad . \quad . \quad (14)$$

The expression for the p_H of a salt derived from a weak base and a strong acid is obtained from equation (13) by exchanging p_{OH} for p_H and p_A for p_B. Thus

$$p_H = 7 - \tfrac{1}{2}p_B - \tfrac{1}{2}\log C. \quad (15)$$

As examples for the application of these formulæ we calcuate the p_H of N/100 solutions of sodium or potassium acetate, and of aniline hydrochloride, taking p_A for acetic acid as 4·75, and p_B for anilinium hydroxide as 9·4. We thus find for the salts of acetic acid $p_H = 7 + 2{\cdot}38 - 1 = 8{\cdot}4$, and for the N/100 solution of aniline hydrochloride $p_H = 7 - 4{\cdot}7 + 1 = 3{\cdot}3$.

Salts derived from Two Weak Components

For the hydrolysis of a salt derived from a weak acid and a weak base we refer to the chemical equation (*C*6), p. 8. Interchanging reactants and resultants, we write

$$B^+ + A^- + H_2O \rightleftharpoons BOH + HA. \quad . \quad (C6a)$$

Using the same notation as before, we have with sufficient

accuracy $[B^+] = [A^-] = C(1 - x)$; $[BOH] = [HA] = Cx$; hence, applying the law of mass action,

$$K_h = \frac{C^2x^2}{C^2(1-x)^2} = \left(\frac{x}{1-x}\right)^2. \quad . \quad . \quad . \quad (16)$$

We see, therefore, that in this case x is independent of the concentration. Expressed in terms of K_h it has the value

$$x = \frac{\sqrt{K_h}}{1 + \sqrt{K_h}}. \qquad (16a)$$

In order to express K_h in terms of the dissociation constants of the weak acid and weak base, and to enable us to calculate $[H^+]$ and $[OH^-]$, we utilize the chemical equations (*C7a*) and (*C7b*), p. 25, and apply the law of mass action, expressing the concentrations in terms of C and x. We thus have

$$K_a = [H^+]\frac{C(1-x)}{Cx}; \quad K_b = [OH^-]\frac{C(1-x)}{Cx};$$

hence

$$K_aK_b = [H^+][OH^-]\left(\frac{1-x}{x}\right)^2 = K_w/K_h$$

and $$K_h = \frac{K_w}{K_aK_b} \qquad (17)$$

Also $$[H^+] : [OH^-] = K_a : K_b. \qquad (18)$$

Effect on Conductivity.

From the chemical equation (*C6a*) it will be apparent that in the present case hydrolysis reduces conductivity since it results only in the formation of undissociated molecules from ions.

Effect on p_H.

Indicating $-\log K_a$ by p_A, $-\log K_b$ by p_B, we have, by equations (8) and (18),

$$p_H + p_{OH} = 14,$$

and $$p_H - p_{OH} = p_A - p_B;$$

hence $$p_H = 7 + \tfrac{1}{2}(p_A - p_B) \quad . \quad . \quad (19)$$

We see from this result that the p_H of the solution of a salt derived from a weak acid and a weak base is independent of concentration. It is greater than 7, i.e. alkaline, when p_A is greater than p_B, or K_a is smaller than K_b, i.e. when the acid is weaker than the base. Conversely, the p_H is smaller than 7, i.e. acid, when the base is weaker than the acid.

The Theory of Indicators and of their Application to p_H Measurement.

An indicator is either a weak acid or a weak base the salts of which have a different colour from the free acid or base. We may therefore distinguish between *acidic* and *basic* indicators. In terms of the ionic theory an indicator is a weak acid, or a weak base, the acidic or basic ion of which has a different colour from the undissociated molecule. So far as chemical equilibrium is concerned, it is indifferent whether the ions have a chemically different constitution from the molecules. It is quite open to us to assume that molecules and ions occur at equilibrium, e.g. both in a benzenoid and a quinonoid form, the benzenoid form preponderating greatly, say, in the molecules, and the quinonoid form in the ions. There would then be an equilibrium of four molecular species. Examination shows (S. T. Acree, *Am. Chem. J.*, 1907, **38**, 1; 1908, **39**, 529. A. A. Noyes, *J. Am. Chem. Soc.*, 1910, **32**, 815) that the conclusions to be drawn are the same as when we simply consider the equilibrium of molecules and ions. We propose to confine ourselves to the consideration of the influence of p_H on the ratio between molecules and ions in

the cases of a univalent acidic and of a univalent basic indicator. We have the equilibrium, either

$$HA \rightleftharpoons H^+ + A^-$$

or

$$BOH \rightleftharpoons OH^- + B^+,$$

applied to which the law of mass action yields respectively the equations

$$[H^+] = K_a \frac{[HA]}{[A^-]}$$

and

$$[OH^-] = K_b \frac{[BOH]}{[B^+]}, \text{ or } [H^+] = \frac{K_w}{K_b} \frac{[B^+]}{[BOH]}.$$

In the case of the acidic indicator, the effect of adding hydrogen ions will thus be to increase the concentration of the molecules HA relatively to the ions A^- and the indicator will show the colour of the former in the more acid solutions, and that of the latter in the more alkaline ones. We may call the molecules the acid, the ions the alkaline form of the indicator. Conversely, the colour of the ion B^+ will be shown by the basic indicator in the more acid solutions, that of the molecules BOH in the more alkaline ones. Here we may call the ions the acid, the molecules the alkaline form of the indicator. If we therefore introduce the following notation:

For the acidic indicator: $[HA] = [Ac]$; $[A^-] = [Alk]$; $K_a = K_i$.

For the basic indicator: $[B^+] = [Ac]$; $[BOH] = [Alk]$; $K_w/K_b = K_i$; we obtain for both types of indicator the equation

$$[H^+] = K_i \frac{[Ac]}{[Alk]}. \tag{20}$$

Introducing as previously the quantities p_H and p_I, the latter defined by $p_I = -\log K_i$, where K_i is measured in mols per litre, we have

$$p_H = p_I + \log \frac{[Alk]}{[Ac]}. \tag{21}$$

This equation contains the most essential information about univalent binary indicators. It shows that so far as reaction to p_H is concerned, there is no difference between an acidic and a basic indicator. Different indicators differ in the value of the constant p_I. When $p_H = p_I$, the concentrations of the acid and alkaline forms of the indicator are the same, and all univalent binary indicators will show the same ratio of [Ac] to [Alk] for the same value of $p_H - p_I$. The equation shows that there is no p_H at which an indicator shows a sudden colour change, but that the latter takes place continuously over a relatively small range. The p_H at which the colour change is most perceptible will in general not be equal to p_I, but will depend *inter alia* on the relative brilliance of the Ac and Alk forms of the indicator. In the case of *phenolphthalein* the Ac form is colourless, and hence the change to pale pink will become visible at a p_H, at which there is a considerable excess of Ac over Alk. The value often given is [Ac]: [Alk] = 20. Thus if we take for phenolphthalein $p_I = 9{\cdot}7$, the colour change would be perceptible at $p_H = 9{\cdot}7 + \log 1/20 = 8{\cdot}4$. Inversely with *methylorange*, the Ac form is more brilliant than the Alk form, and the colour change is believed to be most readily seen, when [Alk] is about ten times [Ac]. Thus taking $p_I = 3{\cdot}3$, the most easily reproducible tint is seen at about $p_H = 4{\cdot}3$.

To decide which indicator to take in the titration of a given weak acid or base by a strong alkali or acid we should refer respectively to equations (14) and (15), p. 35, from which we may calculate the p_H at the end point (equivalence point). As is apparent from the equations, this p_H depends to a small extent on the dilution of the solution, a fact which is, however, usually insufficient to affect the choice of an indicator.

A very important application of indicators is their use in the quantitative determination of p_H. The potentiometric determination of this quantity, which forms an important branch of the subject-matter of this treatise, must be considered the standard method, to which the various colorimetric methods, based on the use of indicators, are subsidiary. Some sources of error are inherent in the indicator method.

Thus the presence of salts, such as NaCl, affects not only the p_H of solutions, as recorded by the hydrogen electrode, but also the readings of indicators, in a manner peculiar to each. Similarly the readings of indicators are affected by the presence of proteins, and we therefore speak of " salt " and of " protein " errors.

A source of difficulty in the use of indicators both for purposes of titration and of p_H measurement is the presence of colour in the solutions to be examined. Two methods are in use for avoiding this difficulty. The first is that introduced by Walpole in 1910. It consists in superimposing on the standard of comparison, a thickness of the solution to be tested equal to that undergoing test, and on the latter a similar thickness of water. In the second method a small thickness of the liquid to be tested, and a high concentration of indicator are employed. For both, standard solutions of known p_H are required. These solutions should be **buffers**, a term introduced in 1900 by Fernbach and adopted by Sørensen and others. It indicates a solution of well-defined p_H, the latter being affected only to a small extent by the addition of acid or alkali. The nature of these solutions will be discussed later. The application of the two methods is illustrated by the B.D.H. Comparator and Capillator respectively. The former (fig. 1, on Plate) comprises a viewing block containing a series of sealed tubes holding buffer solutions of p_H increasing in steps of 0·2. Each buffer solution contains the same amount of indicator, the latter being chosen so that a definite gradation of colour is visible between one member of the series and the next. Fig. 2 shows a horizontal section through the central part of the comparator taken at the level of the three horizontal openings or windows shown in the lid. Three of the test-tubes are filled to a given mark with the sample, indicator solution being added to only one of them by means of a pipette, so as to make the indicator concentration the same as in the standards. The tubes are then arranged as indicated in fig. 2, held towards a source of uniform light, and viewed through the horizontal openings in the direction of the arrow. The positions of the standard buffers

are exchanged systematically until the shade of the sample is intermediate between that of its neighbours. The samples are conveniently inverted when placed for comparison in the comparator block. It will be seen that in each case the light passes through the same thickness of the sample thus eliminating its " body colour ".

In the capillator, the solution to be examined, mixed with a suitable amount of indicator of considerably greater strength than that employed in the comparator, is drawn into a capillary tube and is matched against standards placed in similar capillaries.

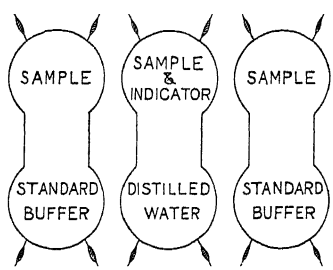


Fig. 2

Another very instructive method of p_H estimation is that due to Gillespie (*J. Amer. Chem. Soc.*, 1920, **42**, 742; *J. Bact.*, 1921, **6**, 399). This method may be usefully employed not only for the determination of p_H but also for that of the p_I or K_i of an indicator. The validity of equation (21), p. 38, is assumed, and the ratio [Alk] : [Ac] of the indicator in the solution under test is determined by matching the colour of the latter against that of two superposed solutions, one of which contains indicator practically only in the form Alk, the other only in the form Ac, but of different strength. For this purpose two test-tubes, one containing buffer solution definitely acid, the other buffer solution definitely alkaline to the indicator, are superposed on each other so as to be

viewed through one of the windows of a comparator block. Two tubes containing the test solution are similarly superposed on each other so as to be viewed through one of the other windows. A suitable number of drops of indicator solution is added to each of the buffers and to each of the test solutions. Further indicator solution is then added in drops to one of the buffers, so as to match the colour of buffer with that of test solutions. By the addition of an equal number of drops of indicator to the test solutions the depth of colour in the test and in the comparison solutions is kept the same. The ratio of drops of indicator in the alkaline buffer solution to that in the acid will equal the ratio [Alk] : [Ac] of equation (21), from which therefore p_H may be calculated if the quantity p_I is known. The latter may be determined if inversely a solution of known p_H is employed as the test solution.

Gillespie made his method more precise by adapting it to the use of colorimeter. For this purpose the plan of varying the concentration of indicator in the comparison buffers was abandoned. Instead, the indicator was made of the same strength in each, as well as in the test solution, but the thicknesses of the comparison solutions were made variable in such a way that their sum was always equal to the thickness of the test solution. Indicating, then, these thicknesses of the Alk and Ac comparison buffers respectively by L_{Alk} and L_{Ac}, we may substitute $L_{Alk} : L_{Ac}$ in equation (21) for [Alk]/[Ac]. Fig. 3 shows the execution of this idea in the Hastings hydrogen ion colorimeter, as constructed by Bausch and Lomb.* In this arrangement provision is also made for the Walpole technique of compensation for colour in the test solution. The apparatus is symmetrical as regards test and comparison solutions. For simplicity of exposition we shall refer to fittings on the left side of the figure by means of the subscript l, to those on the right side by the subscript r. We assume that the comparison buffers are placed on the left side of the figure, one, say the Ac form in the cup B_l, the other, i.e. the Alk form in the flare top cup C_l. The combined thickness of

* The writer understands that the manufacture of the Hastings colorimeter has now been discontinued by Messrs. Bausch and Lomb.

the two layers under observation must be made equal to that of the test solution. This can be attained by raising or lowering the hollow plungers D_l and D_r, the instrument being constructed so that both of these are moved simultaneously by a rack and pinion. The test solution with indicator is usually placed in the auxiliary cup A_r on the right. This is provided with an optically ground glass stopper fitting closely into the top, and thus assuring a constant depth of the test solution. The combined thickness of the two comparison buffers is made equal to this (usually 15 mm.), allowance being provided for the thickness of the bottom of the cup C_l. By racking the flare top cup C_l up or down, a ratio of the thicknesses L_{Alk} to L_{Ac} is obtained, at which the colour of the indicator in the cup A_r is exactly balanced against the combination in the comparison solutions in B_l and C_l. These thicknesses may be read on the instrument. The auxiliary cup A_l on the left is filled with test solution without indicator in order to balance out the body colour of the former, and the cups B_r and C_r on the right are filled with distilled water.

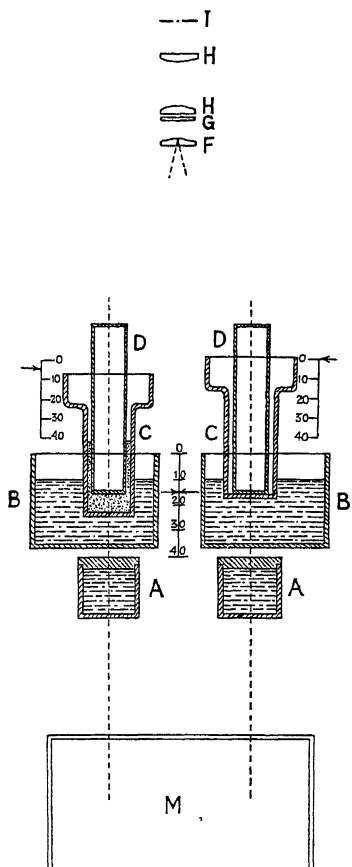


Fig. 3

The optical arrangement is that of the Duboscq colorimeter. An even source of illumination is employed which is obtained from one of the special lamps made for use with the instrument. The light is reflected upwards by the mirror M. After it has passed through the cups, the combination of the rhomboid prisms E, the biprism F and a system of lenses produces two adjacent semicircular images due to test and comparison solutions respectively.

Another method of varying the depth of each comparison solution continuously, while keeping the sum of the depths constant, is to place the two solutions in wedge-shaped vessels, combined to form a single unit as shown in fig. 4. It is clear that, starting from the bottom and viewing the double wedge in the direction of the arrow at successive levels, all shades from the alkaline to the acid colour of the indicator will become visible. If a rectangular trough containing the test solution plus indicator in a thickness equal to that of the combined liquids in the wedges is placed beside these, there will be a level at which test and combined comparison solutions show the identical colour. From the position of this level the ratio [Alk] : [Ac] may be deduced, and hence from equation (21), p. 38, the p_H of the test solution. In the " Hellige Wedge Pehameter " the comparison solutions are gelatinized and placed between two glass plates, on one of which there is a scale calibrated in p_H. The principle of this method of determining p_H is due to N. Bjerrum (Theorie der alkalimetrischen und azidimetrischen Titrierungen. Stuttgart, 1914).

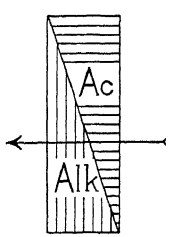


Fig. 4

The Course of Neutralization of a Weak Acid by a Strong Base and the Buffering Power of Solutions.

We have defined a buffer solution as one which shows only a small alteration of p_H on addition of strong acid or alkali (p. 40). The most useful buffer solutions are mixtures of weak acids or bases and their salts, such as are obtained by

the partial neutralization of a weak acid or base. It will be readily understood that in a mixture of a weak acid and its sodium salt the addition of a strong acid or alkali will affect the ratio of the two constituents, with only small alteration of p_H. To follow this alteration more closely, we consider the neutralization of the weak acid HA_w by a strong base as expressed by the equation

$$HA_w + OH^- = H_2O + A_w^-.$$

We assume C original equivalents of the acid given, which have been partially neutralized by the addition of x equivalents of alkali. Strictly, the reaction is reversible, but in the cases under consideration, so long as the concentration of HA_w is appreciable, that of OH^- remains negligible, so that the amount of A_w^- may be considered equal to x, that of HA_w equal to $C - x$. We consider the volume to be unity throughout, thus making amounts equal to concentrations, i.e. $[HA_w] = C - x$; $[A_w^-] = x$. $[HA_w]$, $[A_w^-]$ and $[H^+]$ are subject to the equilibrium $HA_w \rightleftharpoons H^+ + A_w^-$, so that we have

$$K_a = [H^+] \frac{x}{C - x}, \qquad . \quad . \quad (22)$$

or, re-arranging, and taking logarithms,

$$p_H = p_A + \log \frac{x}{C - x}. \qquad . \quad . \quad (22a)$$

Expressing x in terms of the percentage neutralization y, defined by $y = 100x/C$, we have:

$$p_H = p_A + \log \frac{y}{100 - y}. \qquad (22b)$$

This equation shows that the p_H during neutralization of a given weak acid by a strong base depends only on the stage reached (i.e. on the percentage neutralization), but not on the original concentration of the acid; also we see that the neutralization curve of any one acid differs from that of

another only in the value of p_A, and can therefore be derived from it by simple transposition in the direction of the p_H axis. The equation also shows that $p_A - p_H$ has the same value for y, as $p_H - p_A$ for $100 - y$. For half neutralization ($y = 50$), $p_H = p_A$, a relation that can obviously be utilized for the determination, from p_H measurements, of p_A, and hence of the dissociation constant of a weak acid (see also p. 26).

Being based on the approximations that $A_w = 0$ for $x = 0$, and $HA_w = 0$ for $x = C$, equations (22) are obviously not applicable to either of these limits of x. For $x = 0$ we obtain a value, which is sufficiently accurate in most cases, by making use of equation (1*c*), p. 25, and the relation $[H^+] = \alpha C$. Thus, we find by a simple calculation:

$$p_H = \tfrac{1}{2} p_A - \tfrac{1}{2} \log C, \quad . \quad . \text{ (for } x = 0); \quad . \quad (23)$$

and, according to equation (14), p. 35,

$$p_H = 7 + \tfrac{1}{2} p_A + \tfrac{1}{2} \log C. \quad . \quad . \quad \text{(for } x = C) \quad . \quad (24)$$

The difference between these two values, that is the range of p_H travelled during neutralization, is $7 + \log C$, which, it will be noted, is independent of the acid chosen, and also is the same as the range of p_H travelled by a strong acid under similar conditions.

Fig. 5 illustrates what has been discussed. The drawn-out curve A represents the neutralization of acetic acid ($p_A = 4{\cdot}75$) of N/10 strength, the dotted portion referring to a N/100 solution. The greater part of the neutralization curve is common to both solutions. The abscissæ are percentage neutralizations y, the ordinates, p_H values, the scale of which is given on the left.

The **buffering power**, or *buffer capacity*, of a solution we may define as dx/dp_H, where dx is the small amount of strong acid, or $-dx$ the small amount of strong base added (D. D. Van Slyke, *J. Biol. Chem.*, 1922, **42**, 525). We may term dy/dp_H, which compares only buffering of solutions derived from a given original solution of acid, as the *relative*

buffering power of the solution. By differentiating and transposing we find, from equations (22*a*) and (22*b*),

$$\frac{dx}{dp_H} = 2{\cdot}30\left(1 - \frac{x}{C}\right)x \qquad . \; . \quad (24a)$$

and

$$\frac{dy}{dp_H} = 2{\cdot}30\left(1 - \frac{y}{100}\right)y. \qquad (24b)$$

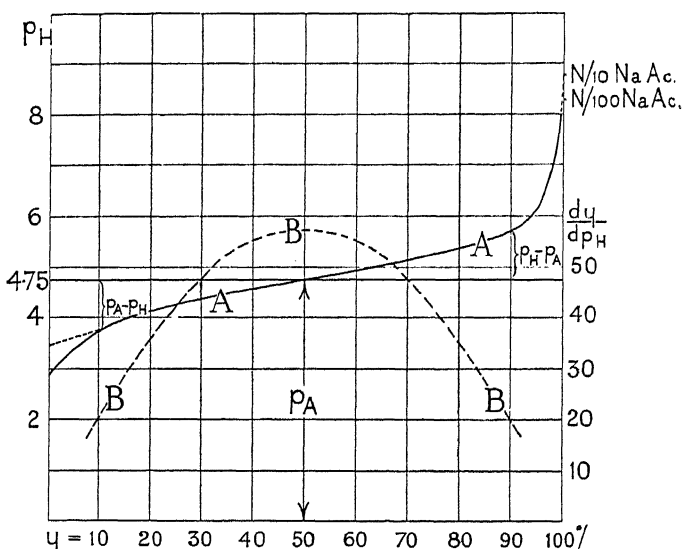


Fig. 5

The curve B, representing the relation between dy/dp_H and percentage neutralization is shown as a broken line in fig. 5. The abscissæ are percentage neutralizations as in curve A, and the ordinates values of dy/dp_H, the scale of which is given on the right side of the figure. It is seen, and can be readily verified from equation (24*b*), that the curve is symmetrical to the half neutralization ordinate, on which it reaches a maximum. A fact closely connected with this is

that the curve A has an inflexion point at half neutralization. At 15 per cent and 85 per cent the buffering power sinks to about half of its maximum value. We see therefore that buffer solutions may be made up usefully from about 15 to 85 per cent neutralization of a weak acid. It follows from equation (24*a*), that at a given stage of neutralization (x/C) buffering power is proportional to the original concentration of the acid. To confirm this, make $x/C = a$, where a is a constant, eliminate the variable x from equation (24*a*), and obtain an expression for the buffering power, in which C occurs as a factor.

It will be seen from fig. 5 that a considerable part of the neutralization curve on both sides of 50 per cent differs little from a straight line. If mixtures of several weak acids of different p_K are suitably chosen, their neutralization curves may be made to merge continuously into each other, so as to yield a single line, which is almost straight. Mixtures of this kind, known as universal buffer mixtures, are obtainable commercially, and are found extremely useful for obtaining buffers of any desired p_H. Examples have been published by Prideaux and Ward (*Trans. Chem. Soc.*, 1924, **125**, 426); by Britton and Robinson (*J. C. S.*, 1931, p. 1456), and by German and Vogel (*Analyst*, 1937, **62**, 271). Accurate instructions for making buffer solutions of desired p_H have been published by various investigators. For details we make reference to W. Mansfield Clark, *The Determination of Hydrogen Ions*, London, 1928. A very useful standard buffer is a 1/20 molar solution of potassium hydrogen phthalate, for which $p_H = 3{\cdot}97$.

Chapter IV

ELECTROMOTIVE FORCE AND HEAT OF REACTION.—THE GIBBS-HELMHOLTZ EQUATION

In this chapter we give an account of the relation between the electromotive force of a reversible galvanic cell and the heat of the underlying chemical reaction. This is a subject of great theoretical importance although it has little direct bearing on electrochemical analysis.

When a Daniell cell is discharging, zinc goes into solution with the formation of zinc ions at the negative pole, while metallic copper is formed from copper ions at the positive pole. The whole process may be expressed by the chemical equation:

$$Zn + Cu^{++} = Zn^{++} + Cu. \quad . \quad . \quad (C8)$$

When a potential difference greater than the E.M.F. of the cell is applied in opposition to the E.M.F., the action is reversed, and the cell is charged. The heat of the reaction on discharge was found by Jahn to be 50,110 calories or $50{,}110 \times 4{\cdot}183 = 209{,}610$ joules.

One of the methods by means of which this value may be found is to place the cell plus its external circuit in an ice calorimeter, and determine the heat produced in the latter, while a measured current is being generated by the cell for a known time. The current may be recorded outside the calorimeter by an instrument, the resistance of which is known, so that a correction for the heat produced in the instrument can be applied if necessary. The heat corresponding to a known number of coulombs, i.e. to a known amount of chemical action, being thus ascertained, the heat corre-

sponding to $2 \times 96{,}500$ coulombs, i.e. the heat of the reaction expressed by the above chemical equation (*C*8), may be calculated.

The E.M.F. of the Daniell cell used was 1·0962 volt. The heat value of the electrical energy corresponding to the passage of $2 \times 96{,}500$ coulombs was thus $2 \times 96{,}500 \times 1{\cdot}0962 = 211{,}570$ joules. It will be seen that this differs from the heat found calorimetrically only by a small amount, being greater than the latter by about one per cent. In this connexion the suggestion was put forward independently by Kelvin (then W. Thomson) and v. Helmholtz that the maximum electrical energy obtainable from a galvanic cell is the exact equivalent of the total energy which is emitted in a calorimeter as heat by the chemical reaction of the cell. This suggestion is not well founded in thermodynamical theory, though it appeared to derive some support from the measurements on the Daniell cell. Later work by Jahn on different cells yielded among others the result that the maximum electrical energy obtainable from a copper, copper acetate, lead acetate, lead cell was about 25 per cent greater than that obtainable calorimetrically from the chemical reaction, whereas in a silver, silver chloride, zinc chloride, zinc cell the position was reversed and the electrical energy was approximately 10 per cent less than the calorimetric energy.

The full thermodynamic theory of energy conversion in the Daniell cell was first given by v. Helmholtz, and the theory of energy conversion in chemical reactions generally by Willard Gibbs. The mathematical expression of these theories is known generally as the Gibbs-Helmholtz equation. To explain this equation we must recapitulate some of the fundamental concepts and theorems of thermodynamics applied to physical and chemical changes.

We start from a system of bodies at a given temperature, which we call *reactants*, and we imagine a change to have taken place converting the reactants into what we shall call *resultants*. We assume reactants and resultants to have the same temperature. Thus the reactant system may have contained 65·4 gm. of metallic zinc plus 63·6 gm. of copper

ions as envisaged by the chemical equation (*C*8) above, and the resultant system these same material units at the same temperature after undergoing the change expressed by the equation.

Application of the First Law of Thermodynamics

Intrinsic Energy.

According to the first law of thermodynamics (law of the conservation of energy) the resultant system differs from the reactant system by a definite amount of energy which is called the difference of *intrinsic* or of *internal energy* between the two states, and which we shall indicate by U (see note).* If the whole of this energy has been converted into heat, which we may indicate by Q_v, then the loss of intrinsic energy equals Q_v, so that

$$-U = Q_v. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Thus the calorimetrically determined heat of the Daniell cell considered above is the negative value of the difference between the internal energy of the resultant $Zn^{++} + Cu$ and the reactant $Zn + Cu^{++}$. For the strict meaning of the experimentally derived quantity as a partial differential quotient the reader is referred to the discussion below, of the free energy changes in a Daniell cell.

Application of the Second Law of Thermodynamics

Available Energy.

Available forms of energy, often referred to as *useful work*, to which the various kinds of mechanical energy and elec-

* It has been advocated that a Δ should always be placed in front of symbols intended to indicate differences in thermodynamic quantities, thus according to this recommendation what we are expressing by U should be indicated by ΔU. For the superfluity of such a practice the reader is referred to a letter published in *Nature*, 1937, **140**, 809.

trical energy belong, are of such a nature that they can be converted into each other, though never completely, yet without assignable limit short of completion. In all "*natural*" processes a certain loss of available energy occurs, which reappears as heat. Thus, by means of mechanical devices the weight of 1 Kgm. falling through 2 m. can be employed to raise a weight of slightly less than 2 Kgm. 1 m. It is, however, never possible for it to raise quite 2 Kgm. by the distance stated; a certain excess of mechanical energy being necessary to supply the driving power. It is impossible to state any general lower limit for the excess, since this depends on the perfection of the mechanical device used, and a limiting process can therefore be envisaged, in which no such excess is employed, and which might proceed just as well in one direction as in the opposite one. Such an imaginary process is generally termed in thermodynamics a "*reversible process*". This latter term is often applied by chemists somewhat loosely also to any *natural* process which can approach the imaginary thermodynamical process indefinitely. For the true thermodynamical reversible process we therefore prefer the term "*equilibrium process*", which indicates that it proceeds always through states of equilibrium.

Heat Energy.

Heat, as such, always tends to flow from higher to lower temperatures, and thus to bring about an equalization of the latter. In order to transfer heat as such to one or more bodies which we may call a system, the temperature being given, it is therefore necessary to have another system of higher temperature which we may call a heat reservoir. The greater the difference of temperature between the heat reservoir and the given system, other things being equal, the more rapid will the transfer of heat be, but no lower positive limit can be assigned to the difference of temperature required. We may therefore imagine heat to be transferred without a difference of temperature, in which case it might just as well flow in one direction as in the opposite one. In this case we

speak of a "*reversible*" in contrast to a "*natural*" heat transfer.

We have seen that all available forms of energy tend to pass into heat. The steam engine has also made us familiar with the fact that heat energy may be converted into available energy. Sadi Carnot first realized the general principles which govern such conversion at the beginning of the nineteenth century, but the full theory was only given later, about the middle of the century by Clausius and by Kelvin (W. Thomson). It was realized by Carnot that for mechanical work to be obtained from heat, the passage of heat from a higher to a lower temperature must take place. The theoretically simplest case is that of two large heat reservoirs I and II (say reservoirs of water), the first at a lower temperature T, the second at a higher temperature $T + \Delta T$. Heat of amount small enough not to affect the temperature of either reservoir is taken from reservoir II and a part of it is given up to reservoir I. This is done by means of a machine working *reversibly*, which as we have said, means working without friction and without temperature gradients. The machine must at the end of the operation be in exactly the same condition as it was at the beginning, or, as it is usually expressed, it must have performed a cycle. Carnot invented a theoretical machine of this kind known as the *Carnot engine*. Its performance is referred to as the *Carnot cycle*. It was shown that the engine produces a definite amount of mechanical work per given quantity of heat transferred from the hotter to the cooler reservoir, and inversely that this same work may be employed to transfer the same heat back from the cooler to the hotter one. Carnot also showed that any other "reversible" engine working between the same temperature limits would have the same efficiency. The law of the conservation of energy was not known to Carnot, who believed that the heat transferred to the cooler reservoir was equal in quantity to that taken from the hotter one. We give the quantitative result recognized as valid at the present day. If $Q + \Delta Q$ is the heat taken from the reservoir II, the absolute temperature of which is $T + \Delta T$, Q the heat delivered to the reservoir I of tem-

perature T, and W the mechanical work obtained from the machine, then

$$W = \Delta Q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and

$$\frac{Q + \Delta Q}{T + \Delta T} = \frac{Q}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

from which, eliminating ΔQ, we find

$$W = \frac{Q}{T} \Delta T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

or, utilizing (3)

$$W = \frac{Q + \Delta Q}{T + \Delta T} \Delta T. \quad . \quad . \quad . \quad (4b)$$

The last two equations become capable of many applications when ΔT and hence ΔQ is assumed to be infinitely small. In this case W becomes infinitely small, and we write for it δW and for ΔT we write δT. Either equation (4*a*) or (4*b*) then yields the differential equation:

$$\delta W = \frac{Q}{T} \delta T. \quad (4c)$$

In this equation δW means the work *obtained* from the engine when the heat Q passes reversibly from the temperature $T + \delta T$ to the temperature T. In our applications we find it more convenient to assign to δW the meaning of the work *imparted* to the engine when the heat Q is transferred reversibly in the opposite direction, i.e. from T to $T + \delta T$. The equation itself remains unaltered. It finds important application in many cycles of the following kind. (1) A finite amount of reactants is transformed reversibly into resultants at the constant temperature T. (2) The resultant system is heated reversibly by the small amount of heat δQ_u to the temperature $T + \delta T$. (3) The resultant system is transformed back into reactants reversibly at the temperature

$T + \delta T$. (4) The reactant system is cooled down again reversibly to the temperature T, thus giving up the heat δQ_a. In such a cycle a *finite* amount of heat Q which may be positive or negative, has been taken from the heat reservoir of temperature T during the transformation of a finite amount of reactants into resultants, and given to the heat reservoir of temperature $T + \delta T$ during the opposite transformation. The work δW imparted to the system is infinitely small, and if *infinitely small* quantities of heat are transferred, δW will be affected only by terms infinitely small of the second order. For this reason the infinitely small amount of heat $\delta Q_u - \delta Q_a$, which is imparted to the system in order to take it from T to $T + \delta T$ and back again need not be considered, and a great simplification thus arises from taking the cycle only over an infinitely small range of temperature.

We sum up as follows. We may apply equation (4*c*) to reversible cycles of the kind we have described. In doing so infinitely small heat terms may be neglected, but work terms must not be neglected unless they are infinitely small, at least of the second order.

Free Energy.

It follows from what has been stated, that in isothermal cycles, i.e. in processes which take place entirely at one temperature and in which all participating systems return to their original condition, no heat can be converted into mechanical or other available work. As Ostwald has put it, a perpetual motion machine of the second order, i.e. one which converts heat of only one temperature into useful work, is impossible. If the isothermal cycles are natural processes, mechanical energy or other useful work will have been converted into heat; on the other hand, if they are reversible processes, neither will heat have been converted into available energy, nor will the reverse transformation have taken place.

If the process is not a cycle, but if reactants have been converted into resultants *isothermally* * *and reversibly*, then simple consideration shows that the available energy and the

* i.e. at constant temperature.

heat taken up have each a definite value, independent of the path pursued. The available energy taken up by the resultants is described as the increase in *free energy* or more fully as their free energy increase according to Helmholtz. The heat taken up is described as the *latent heat* of the resultants or of the process. We shall indicate the free energy increase by F, the latent heat by L. According to these definitions and by the first law, we have:

$$U = F + L, \tag{5}$$

U being the intrinsic energy increase as already defined. It will be noted that in this equation all terms have a value independent of the path followed, U according to the first law, and F and L according to the second. Though the latter two quantities have in all cases a definite meaning, yet they can by no means always be determined in a direct manner, for in order that this may be done true equilibrium conditions must exist, which can be approached indefinitely by natural processes. Instances in which both F and L may be derived directly from experimental results are physical processes such as evaporation and sublimation, whereas cases in which F in particular can be readily determined are those of chemical reactions which proceed in reversible galvanic cells.

The Daniell cell may serve as an example. In it the chemical reaction expressed by the equation (*C*8) takes place in either direction according as to whether the cell is discharging or is being charged. If discharge is opposed by a P.D. exactly equal to the E.M.F. of the cell there is equilibrium; and the voltage between the poles approaches that on open circuit (i.e. the E.M.F. of the cell) continuously as the current passes through zero from one direction to the opposite one. The maximum work which can be *obtained* from the chemical reaction (in equational quantities)* is thus $2 \times 96500E$, E being the E.M.F. of the cell. The free energy change, which is work *imparted*, has the negative value of this. Indi-

* This term may be taken as self-explanatory. It is defined *in extenso* on p. 78.

cating Faraday's constant by F and the valency of the reaction by z, we therefore have in general terms:

$$F = -zFE. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In this equation it is assumed that E remains constant during the period of discharge. Such an assumption can always be made, if the cell is considered so large that changes in the concentrations of reactants and resultants are negligible. For the general consideration of finite cells we can calculate the change of F which we shall indicate by δF, that takes place when the small mass δM, measured in equational units, is transformed from the reactant to the resultant state. δM is thus the increase of the mass M of resultants. We have:

$$\delta F = -zFE\,\delta M,$$

or, proceeding to infinitely small quantities:

$$\frac{\partial F}{\partial M} = -zFE.$$

We see that the quantities in which we are interested chemically are partial differential quotients having the dimension energy per unit mass. The present differential quotient is a function of the concentrations (activities) of the reactant and resultant ions, which can be derived from the principles to be discussed in the following chapters. Similar considerations apply to the functions L and U inasmuch as the chemically important values are partial differential quotients. The thermodynamical relations are in the first instance deduced for the functions themselves. For reasons we do not propose to discuss here the relevant relations hold equally for the partial differential quotients according to mass. For simplicity and for the reason we have just stated it is customary to use the symbols of the functions themselves when strictly, partial differential quotients are involved.

The Peltier Effect in a Galvanic Cell.

We have seen that $zFE = -F$ is in general not equal to $Q_v = -U$ in reversible cells. In many cases, for example

in the Daniell cell, zFE is larger. This means that the maximum amount of energy obtainable electrically from the cell is greater than the energy involved in its chemical process. The excess is taken as heat from the surroundings or from the cell itself, and the latent heat L is positive, which is in agreement with equation (5). Such cells tend to cool down on working, an effect which it should be possible to detect experimentally in cases where L is large as in the copper, copper acetate, lead acetate, lead cell. In the case of those cells in which Q is greater than zFE the effect causes heating. The manifestation of latent heat which produces reversible cooling or heating we may consider to be the " Peltier effect " of the cell.

The Gibbs-Helmholtz Equation.

We now come to the consideration of the relation between L and the temperature coefficient of F. This involves the application of equation (4*c*), and of the reversible cycle considered in connexion with it on p. 54. We take a system containing reactants and resultants through this cycle, and in the first instance we assume the volume to be constant. In stage 1 of the cycle the useful work imparted to the system is F, in stage 3 it is $-(F + \delta F)$, in stages 2 and 4 no work terms occur, so that the total work imparted is $-\delta F$. The heat taken from the temperature T to the temperature $T + \delta T$ in the stages 1 and 3 is L. Substituting into equation (4*c*), transposing, and indicating that T is the only independent variable by the use of the symbol of a partial differential quotient, we obtain the result:

$$L = -T\frac{\partial F}{\partial T}. \qquad (7)$$

We now substitute the value of L just obtained into equation (5), transpose, and find:

$$F = U + T\frac{\partial F}{\partial T}. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This is the Gibbs-Helmholtz equation. If the cycle considered takes place under constant pressure, then work terms due to volume changes enter into the individual items. The sum total of such work terms is $p\Delta v$, where Δv is the total volume change of the cycle. Since this is zero, the total external work performed by means of the system is likewise zero, and equations (7) and (8) remain unchanged. The Gibbs-Helmholtz equation thus holds for reactions taking place either at constant volume or under constant pressure.

Application to a Reversible Galvanic Cell.—We apply the Gibbs-Helmholtz equation to a reversible galvanic cell, expressing U and F in terms of Q and E by means of equations (1) and (6). We thus obtain:

$$L = zFT\frac{\partial E}{\partial T}, \qquad . \quad (9)$$

and

$$E = \frac{Q}{zF} + T\frac{\partial E}{\partial T}. \qquad . \quad (10)$$

Equation (10) is generally referred to as the Helmholtz equation of a galvanic cell.

The Temperature Coefficient of a Galvanic Cell.—From equation (9) it follows, that if L is positive $\frac{\partial E}{\partial T}$ is positive. We have already referred to the fact that if L is positive, the cell on discharging tends to cool down. We may therefore say that if the E.M.F. of a cell increases with temperature, the cell tends to cool down on discharging, and inversely, if the E.M.F. decreases with temperature, the cell tends to heat up. It is not difficult to show that this result conforms to the Le Chatelier principle, i.e. to the requirement of stability in thermodynamic equilibria.

For further remarks on the applicability of constant pressure quantities to the Helmholtz equation the reader is referred to the addenda on p. 128.

Chapter V

ACTIVITY. THEORIES OF INTERIONIC ATTRACTION

The fact has already been referred to on pp. 4 and 5, that interionic attraction vitiates the conclusion drawn from the ionic theory; *firstly*, when thermodynamical deductions are made, which are based on the application of the simple gas laws to the osmotic pressure of the ions; and *secondly*, when it is assumed that *ceteris paribus* current carried is strictly proportional to ionic concentration and to potential gradient. Most of the results of the preceding pages therefore apply only to low ionic concentrations. In the following, a brief sketch will be given of some of the more important modern extensions, having a bearing on the ionic theory.

The Activity Theory.

The Activity theory was introduced by G. N. Lewis in 1908 as a convenient method for expressing thermodynamical results when osmotic pressure and concentration are not correlated accurately by the gas laws.

We start from the thermodynamical result that, when the gas laws hold, the work * to be imparted to a system consisting of two solutions of concentration C and $C + dC$ respectively (both of infinite amount *), when 1 mol of solute is removed by isothermal † and reversible processes * from the first to the second, has the value:

$$dF = RT\frac{dC}{C}. \qquad (1)$$

* For an explanation of the terms "work", i.e. useful work or available energy, "reversible process", and "free energy" the reader is referred to chapter IV, as also for the postulate of an infinite amount of solution.

† i.e. taking place at constant temperature.

This is the **free energy increase** * of the system. If the difference between the concentrations in the two solutions is finite, the first having the value C_1, the second the value C_2, the free energy increase is found by integration to be

$$\Delta F = RT \ln \frac{C_2}{C_1}. \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

By thermodynamical reasoning relations involving ΔF and such colligative quantities as the lowering of freezing-point may be deduced. Similarly ΔF is connected with equilibrium conditions. Making use of such relations it is possible from experimental results to calculate ΔF corresponding to two given concentrations, and then to compare the ratio of these concentrations with that calculated from equation (1*a*). If the gas laws have been obeyed, the two ratios will be the same. In general, however, there will be differences, particularly if the concentrations are appreciable. The differences are very considerable even for quite low concentrations when the solutes are ions.

G. N. Lewis adopted the plan of saving many of the most important relations of physical chemistry by introducing corrected concentrations, which he termed **activities.** They are defined in such a way that they conform accurately to equation (1), and consequently also to (1*a*). The definition of activity, which is usually indicated by the letter a, therefore includes one of the equations:

$$dF = RT \frac{da}{a}, \quad (2)$$

or

$$\Delta F = RT \ln \frac{a_2}{}. \quad (2a)$$

These allow the activity at one concentration to be determined, when that at another is known. In addition, it is necessary to have one fundamental datum. This is so fixed that activity becomes equal to concentration at very low values of the latter in aqueous solutions, i.e. that

$$a : C = 1 \text{ for } C = 0. \quad . \quad . \quad . \quad . \quad (2c)$$

Activities are usually expressed by means of the **activity coefficient** which may be indicated by f, and defined by the equation

$$f = \frac{a}{C}, \quad \text{or} \quad a = fC. \quad . \quad . \quad . \quad . \quad (3)$$

It follows from the thermodynamic deduction of the law of mass action that the latter holds accurately when activities are substituted for concentrations. Thus the simple substitution of a for C in the equations of the previous chapter secures a vast extension of their validity. In a similar way the electrode potential equation discussed in Chap. VI becomes rigorous when a is substituted for C. The alterations to be made in the expressions for osmotic pressure and other colligative properties are, however, not of so simple a nature, and are beyond the scope of this book. It should be noted that Lewis defines C as *molal* concentration or *molality*. This is the number of mols of solute associated with 1000 gm. of water. The difference between molal concentration and molar concentration which is the number of mols contained in 1 litre of solution is so slight in aqueous solutions of low and medium strength as to be of no importance for the purposes of this treatise.

The Interionic Attraction Theory and Activity.

Ionic activities are defined by equation (2*a*) in a manner not differing from that valid for ordinary molecular species, and for strong electrolytes complete ionization at zero concentration is assumed. Thus at zero concentration the activities of the several ions of an electrolyte stand in the ratio of their stoichiometric indices; for example, the activity of potassium ion equals that of chloride ion in extremely dilute potassium chloride solution, whereas in very dilute barium chloride solution the activity of the barium is half that of the chloride ion. It must, however, not be thought that so simple a relation necessarily holds at ordinary concentrations; in fact, it has been shown that the simple relation is probably often departed from.

In dealing with the activities of individual ionic species a difficulty arises in finding methods which will allow the determination of the activity of one ionic species considered separately from that of the species of opposite sign. This is due to the fact that rigorous methods lead in the first instance to the determination of ΔF (equation (2*a*)) for the sum of oppositely charged ions such as those arising from KCl or $BaCl_2$, and additional assumptions not founded on thermodynamics alone are needed before the activities of individual ions can be arrived at. Thus in the first instance it is found possible to determine only products of activities or of powers of activities of the ions associated in a molecular species. To deal conveniently with this matter G. N. Lewis introduced a number of functions, namely, the *mean ion activity*, the *mean ion molality*, and the *mean ion activity coefficient*. A discussion of these is beyond the scope of this treatise, and we content ourselves by referring to Chap. XXVI of Lewis' book on thermodynamics (McGraw-Hill Book Co., 1923).

Of the methods available for the determination of single ion activities we shall mention only the one based on the measurement of electrode potentials, the theory of which is discussed in the next chapter. To obtain the ratio of two ion activities in different solutions by this method, it is in principle necessary to bring the ionic species in question into communication with an electrode reversible to it in each solution, and to connect the two solutions by a junction liquid which shows no potential difference with either solution. The accuracy of the method is therefore limited by the possibility of obtaining a junction liquid of the kind envisaged. Fairly close approximations to this desideratum can be obtained and activities determined, say, for hydrogen ions by the electrode potential method have therefore a sufficient degree of accuracy.

In agreement with its general definition the *activity coefficient* of an ionic species is defined as the ratio of ionic activity to ionic concentration. The concentration here assumed is that arrived at by postulating complete ionization.

Theoretically it can be seen that equation (1*a*) is affected

by interionic attraction in the following way. If C_2 is greater than C_1, ΔF will be smaller than the value given, for interionic attraction will aid the transfer of ions to a more concentrated solution. Furthermore, the effect of interionic attraction will depend only on the concentration of all the ions present, and on the charges following from their valency, but not otherwise on their nature. This is in agreement with a discovery made by G. N. Lewis and Randall in 1921, that the activity coefficient of an ion is a function of the " ionic strength " of the solution only. Ionic strength, which we indicate by I, was defined by the equation

$$I^2 = \tfrac{1}{2}\Sigma(Cz^2),$$

where $\Sigma(Cz^2)$ indicates the sum of the concentrations of every type of ion present, each concentration multiplied by the square of the respective ionic valency z. Ionic strength may be taken as a measure of the intensity of the internal electric field of the solution.

From about the beginning of the present century onwards, a number of investigators, notably Jahn, Sutherland, Bjerrum, Hertz, Milner, Ghosh, and Debye and Hückel have advocated the view that the anomaly of strong electrolytes is due to interionic attraction. Success in obtaining quantitative expressions on kinetic principles has attended particularly the work of Milner and of Debye and Hückel. Strong arguments can be advanced for the view that strong electrolytes, such as NaCl are completely ionized at all concentrations. Thus it is known that crystals of NaCl consist entirely of alternate sodium and chlorine ions held together by electrostatic attraction, and it appears reasonable to believe that a substance which is completely ionized in the solid state should also be completely ionized in solution. Debye and Hückel succeeded in 1923 in deducing an expression for the activity coefficient of an ion, which may be given as follows:

$$-\log f = \frac{Az^2\sqrt{I}}{(\varepsilon T)^{\frac{3}{2}}}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In this equation as before f indicates the activity coefficient, z the valency of the ion, I the ionic strength of the solution, and T the temperature. ε is the dielectric constant of the medium, and A a constant derived from the Avogadro number, the elementary electric charge, and the gas constant. For aqueous solutions at 25° C. the equation reduces to

$$-\log f = 0{\cdot}50z^2\sqrt{I}. \quad . \quad . \quad . \quad . \quad (4a)$$

It will be noted that the experimental discovery of Lewis and Randall that f is a function of the ionic strength is confirmed. The expression (4) has been tested both for aqueous and non-aqueous solutions, and its predictions as regards the influence of valency, ionic strength, and dielectric constant of the medium are verified satisfactorily in solutions not stronger than about 0·01 normal. A somewhat smaller value than that predicted by the formula is, however, generally found for the constant A.

The Interionic Attraction Theory and Conductivity.

The first attempt at a quantitative theory of the effect of interionic attraction on conductivity appears to have been made by Hertz in 1912. The problem was attacked afresh with much success by Debye and Hückel in 1923. The ideas underlying their investigation may be sketched as follows. Two effects have to be considered.

First, the *period of relaxation effect* is connected with the fact that each ion surrounds itself by more ions of opposite than of like charge. The ion is thus embedded in an *ionic atmosphere*, in the centre of which it occupies an average position of equilibrium. When a potential gradient is applied to the solution the ion is moved from its position of equilibrium and an opposing force is brought into being, just as a heavy particle placed at the centre of the earth would be acted upon by gravity when removed from its position of equilibrium. While the ion moves through the solution, its atmosphere moves with it, but there is a certain lag between the two motions, so that the displacement and the opposing force persist. The lag is determined by the so-called period of

relaxation of the atmosphere. The opposing force will increase with increasing period of relaxation. If the latter were zero, there would be no opposing force.

There is a second effect, known as the *electrophoretic effect*, due to the fact that the ion atmosphere with its associated solvent molecules tends to produce a movement of the solution in the opposite direction to the ion under the influence of the applied potential gradient.

Debye and Hückel's formula was improved and simplified in 1926 by Onsager, by considering the joint effects on anion and cation, and by allowing for the thermal motion (Brownian motion) of the ions.

The Debye and Hückel formula as improved by Onsager was deduced for ions of any valency in solvents of any dielectric constant and temperature. We give it here only in the form applicable to a binary univalent electrolyte in aqueous solution at 18° C. It is

$$\Lambda = \Lambda_0 - (0{\cdot}224\Lambda_0 + 50{\cdot}5)\sqrt{C}, \qquad (5)$$

wherein as before Λ is the equivalent conductivity of the electrolyte at the concentration C (in mols per litre) and Λ_0 the corresponding limiting value at zero concentration. It will be seen that $\Lambda_0 - \Lambda$ is proportional to the square root of the concentration, which agrees with a discovery made for extremely dilute solutions by Kohlrausch in 1899. By plotting values of Λ as ordinates against $\sqrt{C}$ as abscissæ, a straight line is thus obtained, the intercept of which on the axis of the ordinates is equal to Λ_0. Having obtained Λ_0, $(0{\cdot}224\Lambda_0 + 50{\cdot}5)$ may be calculated, which should be found equal to the slope of the straight line to the axis of the abscissæ.

The agreement between calculated and experimental slope (in the case of very dilute aqueous solutions of univalent binary electrolytes) is found to be within the limits of experimental error when the necessary correction for conductivity of the solvent is made, thus affording striking proof for the correctness of the theory. At concentrations above about N/500 the concordance begins to break down. The agreement between experiment and theoretical results calculated

for unibivalent salts such as $MgCl_2$ and K_2SO_4 is also satisfactory. In non-aqueous solutions the results for binary univalent electrolytes are not so good, and when the dielectric constant is low the simple Onsager formula breaks down. It is also invalid for aqueous solutions of binary univalent electrolytes such as $MgSO_4$, if complete ionization is assumed.

For weak electrolytes, the modern theories allow corrections to be applied in two directions. First, as regards the dissociation constants, the ionic concentrations may be replaced by activities calculated from the Debye-Hückel formula, the concentration of the non-ionized portion being assumed equal to the activity. Secondly, the mobilities of the ions may be corrected for interionic attraction according to the Onsager formula. The constancy of the dissociation constant is thus improved in all cases. For weak acids like acetic a difference of only a few per cent between the corrected and uncorrected values is obtained, but for stronger acids the difference is very considerable. Tested in this way, bi-bivalent salts turn out to be relatively weak electrolytes. Thus $MgSO_4$ yields a dissociation constant of about 0·007. The view that many of the electrolytes usually considered strong are only partially dissociated is supported by work of C. W. Davies and his collaborators from 1927 onwards. As regards the undissociated molecules, the fact must not be lost sight of that these may very well be simply pairs of ions held together by *electrovalent* as distinct from *covalent* bonds. Some investigators support the view that purely physical theories, which embrace the effect of solvation and of the size of the ions, and from which approximations of a mathematical nature are eliminated, will explain the behaviour of those electrolytes which do not conform to the Onsager equation.

Ohm's Law in very powerful Electric Fields, and in Fields of High Frequency. The Wien and the Dispersion Effect.

The fact that theories of complete ionization lead to the conclusion that there are deviations from Ohm's law in very

powerful fields, and also in very rapidly alternating ones, was first pointed out by the writer in 1923 (*Phil. Mag.*, 1923, **45**, 284). This conclusion appeared to be at variance with the experimental knowledge of the time, and it was thought by the writer to represent an argument against complete dissociation, which might perhaps be overcome by the assumption of firmly bound chains of water molecules, connecting individual ions and involving a non-continuous dielectric constant of the medium. However, since then both classes of phenomenon have been observed.

Deviations from Ohm's law in very powerful fields follow from the recognition of the fundamental fact that the existence of the difference of mobility $\Lambda_0 - \Lambda$ is due to the non-random distribution of the ions. Now Milner pointed out in 1918 (*Phil. Mag.*, 1918, **35**, 353) that the passage of the current through a solution of given concentration will tend to alter the distribution of the ions into a random one, and hence to reduce $\Lambda_0 - \Lambda$. This should become perceptible in very powerful fields. A reduction of $\Lambda_0 - \Lambda$ in very powerful fields, however, means an increase of Λ, and Ohm's law requires that Λ should be independent of the current density. Deviations at very high frequencies, i.e. for very small alternately opposite pulses of current, follow from the conclusion that the ion will assume an average position of equilibrium in the absence of an external field, from which it can be displaced an infinitely small way by an infinitely small force. The presence of other ions can therefore not affect its mobility, if the displacement is small enough. It is only when it has to move a sufficient distance, to pass other ions, that an opposing force, or polarization, is developed. In modern parlance we should say that the force of relaxation can only develop to an appreciable value when the ion has been removed sufficiently from the centre of its atmosphere. It may be objected that the arguments here put forward for the behaviour of an ion in an alternating field would apply equally to the orientation of molecular dipoles in a liquid, and even to the electrons of a non-polar molecule. However, it is manifestly safe to assume that the effect has a

lower order of magnitude in these cases than when we are dealing with free ions separated by many molecular diameters.

The variation in the conductivity of electrolyte solutions in very powerful fields was demonstrated experimentally by Wien in 1927, and is known as the **Wien effect.** The variation in conductivity in alternating fields of very high frequency, known as the **dispersion effect,** has been demonstrated by Sack in 1928, and has since been confirmed in a number of investigations. Both classes of phenomena have thus become important supports of the theory of interionic attraction.

The quantitative theory of the Wien effect was worked out shortly after its experimental discovery by Joos and Blumentritt in 1927, and by Blumentritt in 1928 and 1929. It was shown that in fields up to 25,000 volts per cm. good agreement between theory and experiment exists. The quantitative theory of the dispersion effect was developed by Debye and Falkenhagen in 1928, prior to its experimental demonstration.

The two effects have been brought into close relation with the " radius of the ionic atmosphere ", which has a magnitude of about $10^{-8}/\sqrt{C}$ cm. in aqueous solution at ordinary temperature (the concentration C being given in mols per litre), and with the " period of relaxation ", which is approximately equal to $10^{-10}/C$ sec. under similar conditions. When the distance travelled by the ion under the influence of an applied field of, say, ten to one hundred thousand volts per cm. during the period of relaxation exceeds the radius of the ionic atmosphere, the effect of the latter tends to disappear.

Similarly, when the period of an applied alternating field sinks below the period of relaxation, the dispersion effect makes its appearance.

According to these theories the mobility of the ion in very powerful fields approaches the value which it has at infinite dilution, since in these it frees itself entirely from its atmosphere, and the latter has not time to reform. At infinitely high frequency, however, the ion only becomes free from the relaxation effect; the electrophoretic effect, being a viscosity phenomenon, persists.

Chapter VI

ELECTRODE POTENTIALS. LIQUID JUNCTION POTENTIALS. REVERSIBLE CELLS AND HALF-CELLS. ELECTRODE POTENTIALS OF HALF-CELLS

We begin this chapter by recapitulating some of the considerations of Chap. IV. It will be remembered that a Daniell cell, built up of a copper and a zinc plate each in contact with a solution of its own sulphate, shows a potential difference between its poles on open circuit of a little over one volt. This P.D. we may call the *equilibrium potential* of the cell. If a sufficiently small current is taken from the cell, some copper is deposited on the copper plate, zinc dissolves from the zinc plate, without in either case altering the concentration of the solutions to an appreciable extent, the boundary between the copper and zinc sulphate solutions is slightly displaced, and the total E.M.F. of the cell remains almost unchanged. If the potential difference between the copper and zinc plates is increased slightly above its equilibrium value by means of an applied electromotive force, current flows in the opposite direction, and the processes described are reversed. As stated in Chap. IV, a cell such as the Daniell cell is known as a *reversible cell.* Its electrodes are termed *reversible electrodes.* Passing from the positive (copper) pole of the working cell through the electrolyte to the negative (zinc) pole, the potential differences present are conveniently considered to be (1), the P.D. $Cu - CuSO_4$ solution, in which the copper is considered positive to the solution, the P.D. at the junction between the $CuSO_4$ and the $ZnSO_4$ solutions, and the P.D. $ZnSO_4$ solution $- Zn$, in

which the zinc is considered negative to the solution. In addition to these potential differences, which may be said to be due to electromotive forces, we have in the working cell the P.D. which is required to force the current through the electrolyte according to Ohm's law, and which becomes zero when no current is flowing. The sum total of the E.M.F.s mentioned may be readily measured by connecting a high resistance voltmeter across the terminals of the cell; when, however, we come to the measurement of the single terms of this sum, we meet with considerable difficulties. Various methods are known which might be expected to lead to the evaluation of **electrode potential**, by which we mean the P.D. between the electrode and the adjoining electrolyte. None of these, however, is quite proof to criticism. For practical purposes what is required is a knowledge of the variation of electrode potential, when concentrations in the electrode or electrolyte are varied, or when current is passed across the electrode, and there is no harm in attaching to the electrode potential an unknown constant. It is therefore sufficient to combine each electrode with some well-known and accurately reproducible electrode or half-cell to form a cell, the P.D. across the terminals of which is measured. Such a reference electrode might, for example, as was once suggested, be an amalgamated zinc plate in contact with a zinc sulphate solution of definite concentration. On the recommendation of the Potential Commission of the Deutsche Bunsengesellschaft (1911), it has, however, been decided to refer all electrode potentials to the normal hydrogen electrode, the potential of which is about 0·283 volt positive to the zero value previously in general use. By definition as now accepted the normal hydrogen electrode is one in which hydrogen ions of activity 1 *g*-ion per litre are in thermodynamic equilibrium with hydrogen gas of 1 atmosphere pressure. Such equilibrium may be brought about by means of a platinized platinum or other platinized indifferent conducting plate. Liquid junction potentials are assumed to be absent, or to have been eliminated by calculation, and the temperature of the hydrogen electrode is assumed to be the

same as that of the electrode under measurement. It will be realized that the use of a hydrogen reference electrode or half-cell is attended with difficulties. Experimentally it is not so convenient as certain other half-cells that are commonly employed to replace it. Of these the most important are those in which mercury is in equilibrium with the saturated solution of one of its sparingly soluble salts. Examples of such half-cells are the " saturated ", the " normal ", the " tenth normal " calomel electrode, also the " normal " and the " twice normal " sulphuric acid electrode. In the first, second, and third, mercury is in equilibrium with a saturated solution of mercurous chloride in saturated, in normal, or in tenth normal potassium chloride solution respectively; in the two last named it is in equilibrium with saturated mercurous sulphate in normal or respectively twice normal sulphuric acid. Experimental details regarding the use and preparation of the saturated calomel electrode are given in the section on gravimetric electrolytic analysis. The E.M.F.s e of cells formed by combining the electrodes mentioned with the normal hydrogen electrode at 18° C. are given as follows: for the saturated calomel electrode $e = 0{\cdot}251$ volt, for the normal calomel electrode $e = 0{\cdot}286$ volt, for the tenth normal calomel electrode $e = 0{\cdot}338$ volt, and for the mercurous sulphate normal sulphuric acid electrode $e = 0{\cdot}66$ volt.

The potential of an electrode x referred to the hydrogen electrode as zero is usually expressed by E_h, and termed the hydrogen potential of the electrode. Similarly, when referred to the normal calomel electrode it is given as E_c. Though this method of expression is clear, say, for purposes of tabulation in cases where the nature of the electrode x is independently stated, yet it is open to criticism. Thus the symbol E_c may easily be understood to indicate the potential of the calomel electrode, referred, say, to the hydrogen electrode. This latter potential we shall now express by e_c, indicating at the same time the potential of the electrode x by e_x. Then it is seen that by definition as given above $E_c = e_x - e_c$, and also that the use of the symbol E_c may easily lead to a con-

fusion of signs. We propose to abbreviate $e_x - e_c$ by e_{x-c}, or usually E_{x-c}, and where convenient to use this symbol instead of E_c. Similarly, E_h might be expressed by E_{x-h}, but as we have chosen to make $e_h = 0$, it is simpler to indicate it by e_x or by E_x. In most mathematical equations the nature of the electrode x and that of the reference electrode are irrelevant, so that the subscripts we have discussed may be omitted. Indicating quite generally the P.D. between the poles of a chain formed by combining the half-cells x and y by E_{x-y}, we have the general relations:

$$E_{x-y} = E_{x-a} + E_{a-b} + E_{b-y},$$

and

$$E_{x-y} = -E_{y-x}.$$

Thus the potential E_{x-c} of the electrode x referred to the normal calomel electrode is calculated as follows, if its potential E_x referred to the hydrogen electrode is known:

$$E_{x-c} = e_x - e_c = E_x - 0{\cdot}286 \text{ volt}.$$

At this point it is necessary to interpose some remarks about the *sign* of electrode potentials. By tradition an element is described as electropositive if it has a great tendency to discharge positive electricity in the form of ions into a solution with which it is in contact. To this tradition we propose to adhere in the present treatise. In discharging positive electricity into the solution the element which may be considered to form an electrode becomes negative; thus a zinc electrode in equilibrium with a solution containing zinc ions is more electronegative to the solution than an electrode of less electropositive copper under corresponding conditions. This fact led the older electrochemists to adopt the practice of giving to electrode potentials their opposite sign, a fact which must be remembered by those reading the older literature. It is obvious that a practice of this kind is likely to cause unnecessary difficulty and confusion, and the practice was later dropped. Unfortunately some writers have recently revived the practice, and it therefore becomes necessary to state specifically that in this treatise we define **electrode**

potential as the difference of potential between the electrode under consideration and the reference electrode. When for any reason it is more convenient to state its negative value, i.e. the difference of potential between the reference or auxiliary electrode and the electrode under consideration, we shall refer to it as the **auxiliary potential.**

Oxidants and Reductants. Electrode Reactions and Equations.

The chemical change taking place in the Daniell cell may be expressed by the equation $Zn + Cu^{++} \rightleftharpoons Cu + Zn^{++}$, which must be taken from left to right when the cell is discharging, and from right to left when it is being charged. In the former case zinc is being " oxidized " and copper " reduced ", in the latter it is the copper that is " oxidized " and the zinc that is " reduced ". It will be seen that " oxidation " is accompanied by the assumption of positive charges, " reduction " by their loss. In a similar way the process $H_2 + Cl_2 \rightleftharpoons 2H^+ + 2Cl^-$ may be realized by a cell in which hydrogen and chlorine respectively are brought into communication with a solution of hydrogen chloride by means of platinized platinum electrodes. Here, when the cell is discharging, the hydrogen molecule is being oxidized by the assumption of positive, and the chlorine molecule reduced by the assumption of negative charges; when the cell is being charged, the position is reversed. It is customary, therefore, to term the assumption of a positive charge or loss of a negative one " oxidation ", the assumption of a negative charge or loss of a positive one " reduction ", and to consider positive ions, oxidation products, negative ions, reduction products of the respective molecules or radicals, and vice versa.

In practice the formation of positive ions will usually be accompanied by that of equally and oppositely charged negative ones, since otherwise the bodies as a whole would become heavily charged. Thus in a galvanic cell the passage of electricity from one electrode to the adjoining solution is usually accompanied by the passage of an equal amount from the solution to the other electrode. It is, however, quite

possible to envisage the passage of a quantity of electricity from an electrode of, say, one centimetre area into the adjoining electrolyte so small that not only the material concentrations in the solution but also the electrical condition of the electrode and of the electrode layer remain unaffected to a measurable extent. We may therefore consider the theory of electrode potential, i.e. of the difference of potential between an electrode and the adjoining electrolyte, independently of any other electrode.

Electrode equations express the material changes that take place when the unit of electricity passes from the electrode to the electrolyte. The most convenient unit appears to be the **Faraday** of positive electricity, which was formerly almost universally employed. As previously, we indicate it by F. As typical examples of electrode equations we take the following:

$$\mathrm{Ag} + F \rightharpoonup \mathrm{Ag^{+}}, \quad . \quad . \quad . \quad . \quad (C9)$$
$$\mathrm{Cu} + 2F \rightharpoonup \mathrm{Cu^{++}}, \quad . \quad . \quad . \quad . \quad (C10)$$
$$\mathrm{H_2} + 2F \rightharpoonup 2\mathrm{H^{+}}, \quad . \quad . \quad . \quad . \quad (C11)$$
$$2\mathrm{Cl^{-}} + 2F \rightharpoonup \mathrm{Cl_2}, \quad . \quad . \quad . \quad . \quad (C12)$$
$$\mathrm{Fe^{++}} + F \rightharpoonup \mathrm{Fe^{+++}}, \quad . \quad . \quad . \quad (C13)$$
$$\mathrm{Sn^{++}} + 2F \rightharpoonup \mathrm{Sn^{++++}}, \quad . \quad . \quad . \quad (C14)$$

By equation ($C9$), the arrow being taken from left to right, the fact is expressed that one faraday of positive electricity passes from the electrode to the electrolyte with the conversion of 1 gm. atom of silver into 1 gm. ion of the same element, the electrode thus being the cathode. According to ($C11$), in a similar way, 2 gm. of hydrogen gas become hydrogen ions; according to ($C12$), 2 gm. ions of chloride ion are converted into one mol of the element; and according to ($C14$), 1 gm. ion of stannous is converted into stannic ions. A reversal of the arrow expresses the reversal of the current, and also of the chemical process, the electrode thus being the anode. In order that the postulate we made, that both electrical and material conditions shall remain sensibly unaltered by the transfers contemplated, the electrode would have to be of astronomical dimensions. This might be objected to; our

postulate may, however, be met for ordinary electrodes by multiplying all terms of the equations by a quantity δM, which may be taken as small as desired, provided that it remains large compared with $1/N$, where N is Avogadro's number of 6×10^{23} molecules per mol. In the light of our previous discussion, we may conveniently term the species on the left side of our electrode equations **reductants**, those on the right side **oxidants**. Indicating the former by Re_1, Re_2, &c., the latter by Ox_1, Ox_2, &c., their coefficients respectively by r_1, r_2, o_1, o_2, &c., and the coefficient of F by n, we may express an electrode reaction in general terms as follows:

$$r_1Re_1 + r_2Re_2 + \ldots + nF \rightleftharpoons o_1Ox_1 + o_2Ox_2 + \ldots \quad (C15)$$

In recent years it has become common to express electrode reactions in terms of single molecules, ions, and electrons, instead of g-molecules and g-ions. If ϵ indicates an electron, the above equation is written:

$$o_1Ox_1 + o_2Ox_2 + \ldots + n\epsilon \rightleftharpoons r_1Re_1 + r_2Re_2 + \ldots \quad (C15a)$$

It will be seen that the two notations are readily interconvertible. The electronic form ($C15a$) of equation ($C15$) is often useful for expressing the interaction of single atoms and electrons in terms of contemporary theory. Relations we are usually interested in are, however, thermodynamical, and refer to large numbers of molecules and ions; further, the unit of potential is based on the positive unit of electricity. We propose, therefore, to adhere mainly to the older notation in expressing electrode reactions. It is important to note that it is only when an electrode process may be expressed by an equation as a reversible reaction that we may expect definite values for electrode potentials.

The Dependence of Electrode Potentials on Concentrations (Activities).

The theory of the dependence of electrode equilibrium potential on concentrations is analogous to that of equilibrium in homogeneous systems, and may be looked upon as an

extension of it. As an example we consider the case of a rod of copper which is in equilibrium with a solution containing copper ions according to the equation $Cu + 2F \rightleftharpoons Cu^{++}$, or $Cu - 2\varepsilon \rightleftharpoons Cu^{++}$. This equilibrium may be considered to have been established as the result of two opposite processes. When the electrode reaction proceeds from left to right, copper atoms and positive electricity leave the electrode and enter the solution as positive ions, thus causing the electrode to be charged negatively, or, expressing the same thing in terms of electrons, positive copper ions enter the solution from the electrode, leaving their discarded electrons to charge it negatively. The negative charge of the electrode will hold the positive ions emitted into the solution in close proximity, and thus an electrical **double layer** will be formed, the charge of which will oppose and slow down the process which has produced it, at the same time accelerating the opposite process, expressed by the electrode equation, taken from right to left. This opposite process must be assumed to take place simultaneously, tending to produce a double layer of opposite sign to the one just considered. Equilibrium between the opposing processes is established practically instantaneously, when their rates have been equalized owing to the intervention of the double layer. The latter may consist of either a negative or a positive charge on the rod, and a corresponding excess of positive or negative ions in immediate proximity in the solution. Other electrode reactions may be considered to be analogous. Thus if we dip a platinum plate into a solution containing ferrous and ferric ions, equilibrium may be considered to be established by the intervention of a double layer, which has been formed by ferric ions giving up positive charges to the plate, i.e. taking electrons from it, and thus producing ferrous ions. The double layer will then consist of a positive charge on the plate and a negative one in the solution immediately adjacent.

We revert now to the general equation:

$$r_1\mathrm{Re}_1 + r_2\mathrm{Re}_2 + \ldots + nF \rightleftharpoons o_1\mathrm{Ox}_1 + o_2\mathrm{Ox}_2 + \ldots \quad (C15)$$

We consider first a system in which all activities (concentra-

tions) are unity, and in which the electrode potential difference is zero. Such a system, as we have seen, will in general not be in equilibrium. We may, however, imagine an appliance in which " equational " quantities of reactants are converted isothermally and reversibly into resultants. Such an imaginary appliance, in which all transformations take place at constant temperature, and only through intermediate equilibrium states, we may term an " *equilibrium box* " (Van't Hoff). By " equational " quantities we mean the quantities in grams expressed by the electrode equation, and it is assumed that the electrode is so large that all concentrations and electrical conditions remain unaltered (*vide supra*). According to thermodynamical principles, an amount of mechanical or other " available " form of energy is obtained in such a transformation, which has a *definite value*, that we may indicate by $\bar{A}_0$. It may be either positive or negative, and may be said to measure the " *affinity* " of the process. In a similar way, if the activities have the values $\{Re_1\}$, $\{Re_2\}$. . . $\{Ox_1\}$, $\{Ox_2\}$, &c., the electrode potential still being zero, a different amount of mechanical or available energy is obtained, which we indicate by $\bar{A}$. By familiar thermodynamical reasoning the two quantities are shown to be related by the equation:

$$\begin{aligned}\bar{A} &= \bar{A}_0 + r_1 RT\ln\{Re_1\} + r_2 RT\ln\{Re_2\} + \ldots \\ &\quad - o_1 RT\ln\{Ox_1\} - o_2 RT\ln\{Ox_2\} - \ldots \\ &= \bar{A}_0 - RT\ln\frac{\{Ox_1\}^{o_1}\{Ox_2\}^{o_2}\ldots}{\{Re_1\}^{r_1}\{Re_2\}^{r_2}\ldots}, \quad \ldots \quad (1)\end{aligned}$$

use being made of the theorem, that the work required to remove one mol of solute from a solution in which its activity is unity, to one in which it is a, is given by the expression $RT\ln a$. If the electrode potential has a value different from zero, which we may indicate for the two isothermal and reversible changes considered by E_0 and E respectively, we shall obtain, in addition to the work $\bar{A}_0$ and $\bar{A}$ respectively, the equivalent of the electrical work nFE_0 and nFE respec-

tively. If E_0 and E are equilibrium potentials, then by thermodynamical principles the total work obtained, or otherwise expressed, the total affinity of the process, is zero. We therefore have the two equations:

$$\bar{A}_0 + nFE_0 = 0, \tag{2}$$

and

$$\bar{A} + nFE = 0. \tag{3}$$

Eliminating $\bar{A}_0$ and $\bar{A}$ from equations (1), (2), and (3), and transposing, we find:

$$E = E_0 + \frac{RT}{nF} \ln \frac{\{\mathrm{Ox}_1\}^{o_1}\{\mathrm{Ox}_2\}^{o_2} \cdots}{\{\mathrm{Re}_1\}^{r_1}\{\mathrm{Re}_2\}^{r_2} \cdots} \tag{4}$$

This fundamentally important equation calls for a few remarks. Being deduced thermodynamically, it may be considered free from error in its present form. If it is to be applied, the activities contained in it must be known, and inversely it may be employed for the experimental determination of activities. For many purposes we may, however, simply replace the activities by concentrations, and in the present treatise we propose to do this in future. We shall therefore replace the { } by the [] bracket. Similarly, the constant E_0 will be used to designate the electrode potential when all concentrations are unity. It is a constant which is characteristic of the particular process expressed by the electrode equation (*C*15), p. 76, and is known as the **standard equilibrium** or **standard electrode potential** of the process. By definition it is the P.D. between the electrode and the adjoining liquid, but obviously a constant may be added on each side of the equation, making E and E_0 the P.D.s between the electrode and any standard reference electrode, provided that liquid boundary potentials may be ignored. E_0 is not independent of temperature, but in actual fact the effect of temperature is small and is frequently ignored. Substituting the appropriate values for R and F in equation (4), introducing common in place of natural

logarithms, and making the change from activities to concentrations, we find:

$$E = E_0 + 0{\cdot}000198\,\frac{T}{n}\log\frac{[\mathrm{Ox_1}]^{o_1}[\mathrm{Ox_2}]^{o_2}\ldots}{[\mathrm{Re_1}]^{r_1}[\mathrm{Re_2}]^{r_2}\ldots}\ \text{volt.} \quad (4a)$$

For ordinary temperature we may take $T = 290$, and hence

$$0{\cdot}000198T = 0{\cdot}058\ \text{(volt)}. \quad \ldots \quad (5)$$

We now apply equations (4*a*) and (5) to the electrode equations (*C*9) to (*C*14) of p. 75, and obtain for ordinary temperature:

$$E = E_0 + 0{\cdot}058\log[\mathrm{Ag^+}]\ \text{volt}, \quad \ldots \quad (6a)$$

$$E = E_0 + 0{\cdot}029\log[\mathrm{Cu^{++}}]\ \text{volt}, \quad \ldots \quad (6b)$$

$$E = E_0 + 0{\cdot}029\log\frac{[\mathrm{H^+}]^2}{[\mathrm{H_2}]}$$

$$= E_0 - 0{\cdot}029\log[\mathrm{H_2}] + 0{\cdot}058\log[\mathrm{H^+}]\ \text{volt}, \quad \ldots \quad (6c)$$

$$E = E_0 + 0{\cdot}029\log\frac{[\mathrm{Cl_2}]}{[\mathrm{Cl^-}]}$$

$$= E_0 + 0{\cdot}029\log[\mathrm{Cl_2}] - 0{\cdot}058\log[\mathrm{Cl^-}]\ \text{volt}, \quad \ldots \quad (6d)$$

$$E = E_0 + 0{\cdot}058\log\frac{[\mathrm{Fe^{+++}}]}{[\mathrm{Fe^{++}}]}\ \text{volt}, \quad \ldots \quad (6e)$$

and

$$E = E_0 + 0{\cdot}029\log\frac{[\mathrm{Sn^{++++}}]}{[\mathrm{Sn^{++}}]} \quad \ldots \quad (6f)$$

In equations (6*c*) and (6*d*) the gaseous concentrations $[\mathrm{H_2}]$ and $[\mathrm{Cl_2}]$ occur. Since these are proportional to the pressures of the gases, we may measure the latter by the former, and ascribe to $[\mathrm{H_2}]$ and $[\mathrm{Cl_2}]$ the meaning of pressures. E_0 then becomes the electrode potential, when the gaseous pressure and ionic concentration are unity. An example of the calculation of the effect of pressure on electrode potential is given in Book V.

The quantitative dependence of the E.M.F. of a reversible cell on the concentrations of the active components, on the

affinity of the reaction, and on its equilibrium constant was first investigated by Van't Hoff in a paper presented to the Royal Swedish Academy of Science in 1885. In this paper neither single electrode potentials nor the diffusion potential gradients due to concentration gradients in the solution were considered. The theory of single electrode potentials was given by Nernst in 1888–9, and is commonly associated with his name under the title of *osmotic theory of current production*. We give the following outline of this theory applied to the Cu : Cu^{++} electrode potential at ordinary temperature (17° C.). We revert to equation (6*b*), and note that since osmotic pressure is proportional to concentration we may substitute for $[Cu^{++}]$ the osmotic pressure p of the copper ions, E_0 being then the electrode potential for unit osmotic pressure of the copper ions. We now define a new constant P in terms of E_0 by the equation $E_0 = -0{\cdot}029 \log P$. Substituting in (6*b*), we obtain

$$E = -0{\cdot}029 \log \frac{P}{p} \text{ volt.}$$

This is the Nernst formula applied to the Cu : Cu^{++} electrode. The constant P is called the **electrolytic solution pressure** of the copper. It may be defined as the calculated osmotic pressure of copper ions, which would make the electrode potential zero. For copper the solution pressure is given as $4{\cdot}8 \times 10^{-20}$ atmosphere, for zinc as $9{\cdot}9 \times 10^{18}$ atmospheres, leading to a ratio of about 2×10^{38}. It may be doubted whether the tendency of metals to ionize is not expressed better by their solution "affinity" $\bar{A}_0 = -nFE_0$, equation (2), p. 79, which would not lead to extravagant ratios. It must not be forgotten that to obtain numerical values for either solution affinity or solution pressure an arbitrary assumption as to the absolute value of electrode potential must be made, and it is therefore only differences that have a precise meaning in the case of affinities, and ratios in the case of pressures. The electrode equation (4), p. 79, is frequently referred to as Peters' equation (R. Peters, *Z. Elektrochem.*, 1898, **4**, 534).

Another function which possesses similar characteristics to

solution pressure, and which has found favour in recent years, is **electron activity**. We indicate this function by the symbol $\{\varepsilon\}$, and define it by the equation

$$\{\varepsilon\} = e^{-(FE/RT)} \quad \text{or} \quad E = -\frac{RT}{F}\ln\{\varepsilon\}.$$

Substituting E in equation (4), p. 79, we find:

$$\frac{\{\mathrm{Re}_1\}^{r_1}\{\mathrm{Re}_2\}^{r_2}\ldots}{\{\mathrm{Ox}_1\}^{o_1}\{\mathrm{Ox}_2\}^{o_2}\ldots\{\varepsilon\}^{n}} = e^{nFE_0/RT} = \text{constant}.$$

This equation shows us that we may apply the law of mass action to the electron of the chemical equation (*C*15*a*), p. 76, if we use the function " electron activity " as defined above in the same way as we employ the activities of the ordinary molecular or ionic species. The fact must, however, not be lost sight of that the concept of electron activity is a " derived " one, and that any attempt to employ it to obtain the electrode equation (4) by short cuts must lead to unsound and unsatisfactory deductions.

Liquid-liquid (Diffusion) Potentials. The Dependence of Potential Gradient on Concentration Gradient.

The theory of the dependence of potential gradient on concentration gradient in electrolytes was first given by Nernst in 1888. As we shall see, the subject is closely associated with the theory of diffusion in electrolytes. Potential differences in liquids are therefore frequently referred to as diffusion potentials.

We confine ourselves to binary electrolytes. To fix our ideas, we imagine a dilute solution of hydrochloric acid floated on the top of a more concentrated one in a jar, but will ascribe to each ion the valency n instead of 1 as in the case chosen. In course of time a uniform concentration gradient will have established itself everywhere. We consider unit area of a section in the electrolyte at a distance l from the bottom, at which there is a uniform concentration C, and a concentration gradient in the direction of increasing l of dC/dl (in

the case considered it is negative). This concentration gradient may be considered to exert a pull per g-ion in the direction of increasing l of $-\frac{RT}{C}\frac{dC}{dl}$; for we conclude from equation (1), p. 60, that the maximum work obtainable from the transfer of 1 mol solute from the concentration C to the concentration $C + dC$, i.e. in this case over the distance dl, is $-\frac{RT}{C}dC$. Under the influence of this pull there is a tendency of the ions having the greater mobility (in the present case the hydrogen ions) to get slightly ahead of those having the smaller mobility (the chlorine ions). Thus a potential gradient dE/dl (in the case considered, positive) is established, which will hinder the motion of the more rapid ion and promote that of the slower one. As we are considering a stationary state in the absence of current, the same number of equivalents of positive as of negative ions cross unit section down the concentration gradient per unit of time. In the present case only one kind of each ion has to be considered, and the velocity c of each in the direction of decreasing concentration is the same. Now by definition the velocities of our ions under the influence of unit gradient of potential are $-u_k$ and $+u_a$. Remembering that unit potential gradient exercises a unit force or pull on a unit charge down the gradient, and hence a pull of nF units on a g-ion, we recognize that unit force gives the ions an absolute velocity of u_k/nF and u_a/nF respectively. These quantities multiplied by the total pull per g-ion in the direction of increasing l will give us the actual velocity c of each type of ion. Since, however, c is the same for positive and negative ions in the case considered, and the pull per g-ion on the former is $-\frac{RT}{C}\frac{dC}{dl} - nF\frac{dE}{dl}$, and that on the latter $-\frac{RT}{C}\frac{dC}{dl} + nF\frac{dE}{dl}$, we have

$$\therefore = \frac{u_k}{nF}\left(-\frac{RT}{C}\frac{dC}{dl} - nF\frac{dE}{dl}\right) = \frac{u_a}{nF}\left(-\frac{RT}{C}\frac{dC}{dl} + nF\frac{dE}{dl}\right) \qquad (7a), (7b)$$

or
$$\frac{dE}{dl} = \frac{-u_k + u_a}{u_k + u_a} \frac{RT}{nFC} \frac{dC}{dl} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This result shows in agreement with the principles from which it was deduced that a diffusion potential gradient is dependent for its existence on the difference between the migration velocities of positive and negative ions. It is also seen that diffusion potential is inversely proportional to concentration.

From equations (7*a*), (7*b*), and (8) an expression for the diffusion coefficient of the electrolyte may be readily deduced. If ϕ indicates the " flow " of solute, i.e. the mols of solute that cross unit sectional area per unit of time, then

$$\phi = cC.$$

Eliminating from this, and from equations (7) and (8), c and dE/dl, we obtain after simplification:

$$\phi = 2 \frac{u_k u_a}{u_k + u_a} \frac{RT}{nF} \left(- \frac{dC}{dl} \right). \quad (9)$$

By the definition of a diffusion coefficient, the coefficient of $-dC/dl$ is the diffusion coefficient of the electrolyte. This formula, also due to Nernst, which connects quantities taken from different branches of physical chemistry, has been found in good accord with experimental fact for univalent ions.

We return to equation (8), which can be readily integrated, if we assume u_k and u_a independent of C. We find for the potential difference between the finite concentrations C_1 and C_2:

$$E_{1,2} = \frac{-u_k + u_a}{u_k + u_a} \frac{RT}{nF} \ln \frac{C_1}{C_2}. \quad . \quad (10)$$

Equation (10) may be combined with the electrode equation for a Cu : Cu^{++} or similar electrode, to obtain the total E.M.F. of a combination, in which the metal electrodes 1 and 2 are in equilibrium with solutions of their ions of the concentration C_1 and C_2 respectively, the solutions being in com-

munication with each other. Thus by simple addition of three potential differences, we obtain

$$E_{1,2} = \frac{2u_a}{u_k + u_a} \frac{RT}{nF} \ln \frac{C_1}{C_2}, \qquad (11)$$

an equation which may also be readily deduced by equating the maximum work produced electrically by the cell during the discharge of F coulombs with the maximum work obtainable from the transference of the appropriate quantity of ions from a concentrated to a dilute solution of the electrolyte.

Elimination of Diffusion Potentials.

We now consider the effect of the presence of a second electrolyte of high uniform concentration on the diffusion potential gradient we have just investigated. We take as an example a concentrated solution of KCl of uniform concentration on which is superposed a solution of HCl having a concentration gradient. As we have seen, the hydrogen ion will tend to travel rapidly down the concentration gradient, building up an opposing potential gradient, until in the absence of current the algebraic sum of positive and negative charges crossing any section down the concentration gradient per unit of time has become zero. Owing to the presence of the large excess of KCl, this is attained across all sections by a very small displacement of the K^+ and Cl^- ions, and no appreciable diffusion potential is built up. The motion of the hydrogen ion is also not hindered to any appreciable extent, and it travels more rapidly than it would in the absence of the KCl, and practically at the rate imposed upon it by the concentration gradient alone. We thus see that concentration gradients of one electrolyte in the presence of a large excess of another of uniform concentration are incapable of building up potential gradients to any appreciable extent. Let us now consider a junction of a dilute solution of any electrolyte with a concentrated solution of KCl. Both electrolytes will build up concentration gradients at the junction, but even in those

parts of the junction where the concentration of the KCl is low, we may assume that its concentration gradient will be greater than and swamp that of the other electrolyte. It is thus only the concentration gradient of the KCl that need be considered. We have seen, however, that the potential differences produced by concentration gradients are proportional to the difference of the mobilities of the two ions. In the case of potassium chloride the mobilities of the two ions are sensibly equal, and hence no appreciable potential difference arises from the concentration gradient between the concentrated solution of potassium chloride and the other solution.

The foregoing forms the explanation of a very important suggestion made by Nernst for the practical elimination of diffusion potentials. According to this, there is interposed between the two electrolytes a concentrated solution of potassium chloride or of another electrolyte having an anion and cation of the same mobility. Such another electrolyte proposed by Cumming is ammonium nitrate.

The General Problem of Boundary Potentials.

The general problem of the diffusion potential at the junction of two electrolytes is a difficult one. This is due to the fact that a theoretically sharp boundary is essentially unstable, since it would lead to infinite concentration gradients and hence theoretically to infinite forces, bringing about the destruction of the boundary. More or less arbitrary assumptions must therefore in all cases be made regarding the nature of the boundary. We confine ourselves to the following references: Planck, *Ann. Physik. u. Chem.*, 1890, **40**, 561. Johnson, *Ann. Physik.* 1904, **14**, 995. Henderson, *Z. phys. Chem.*, 1907, **59**, 118; *ibid.* 1908, **63**, 325. Cumming, *Trans. Faraday Soc.*, 1912, **8**, 86. Cumming and Gilchrist, *ibid.* 1913, **9**, 174. Fales and Vosburgh, *J. Am. Chem. Soc.*, 1918, **40**, 1291.

In conclusion we record an expression for the diffusion coefficient of a single cation such as the hydrogen ion when, as in the case we have just considered, it is, owing to the

presence in uniform concentration of a large excess of other ions, under no appreciable electrical constraint. The result is the same as that for a single electrolyte the velocities of whose ions are equal. Indicating the diffusion coefficient by D, we therefore deduce from equation (9):

$$D = \frac{u_k RT}{nF}. \qquad (9a)$$

A corresponding result follows for the diffusion coefficient of an anion. In equations (9) and (9*a*) u_k and u_a may be expressed in terms of l_k and l_a by means of equations (6*a*) and (6*b*), p. 20. For R its value in joules per degree and mol (8·32) must be taken if the other quantities are expressed in customary units.

The Determination of Transport Numbers from E.M.F. Measurements. The Determination of Minute Ionic Concentrations and of Ionic Products.

It will be evident that the possibility of constructing a cell which is independent of diffusion potentials furnishes us with a method for determining transport numbers by means of E.M.F. measurements. Let us imagine that we have constructed a galvanic chain consisting of two half-cells, in each of which an electrode of the same metal is in equilibrium with its ions, the concentration (activity) of the latter being C_1 and C_2 respectively, and let us further imagine that we have brought these half-cells into communication by means of a concentrated solution of either potassium chloride or ammonium nitrate. The E.M.F. of such a chain is given by the equation

$$E_{1,2} = \frac{RT}{nF} \ln \frac{C_1}{C_2}. \qquad (11a)$$

If, on the other hand, we bring the half-cells into communication by means of a solution of the salt of the metal itself, the E.M.F. of the chain is given by equation (11), p. 85. Let us indicate the E.M.F.s thus measured without and with

diffusion potential by E_0 and E_d, then by dividing equation (11) by equation (11*a*) and transposing, we find the transport number of the anion T_a to be

$$T_a = \frac{u_k + u_a}{} - \frac{1}{2}\frac{E_d}{E_0}$$

It will also be readily understood that the theory of concentration cells furnishes a useful means of determining minute ionic concentrations and hence of calculating ionic products (p. 27). We take as a first example the determination of the ionic concentration of hydrogen ion in an N/100 solution of NaOH, and hence of the ionic product of water. We construct a galvanic combination of the following parts: (1) A half-cell containing a hydrogen electrode in N/100 HCl, (2) a similar half-cell containing a hydrogen electrode in N/100 NaOH, (3) a bridge connecting the two containing saturated KCl solution. We then measure the E.M.F. of this combination at ordinary temperature. If the hydrion concentration in the first half-cell is indicated by $[H^+]_1$ that in the second by $[H^+]_2$, then the E.M.F. is given by

$$E_{12} = 0{\cdot}058 \log \frac{[H^+]_1}{[H^+]_2} \text{ volt},$$

$$\text{or } \log [H^+]_2 = -\left(\frac{E_{12}(\text{volt})}{0{\cdot}058} - \log [H^+]_1\right).$$

Assuming the hydrogen chloride in solution 1 to be completely ionized, $[H^+]_1 = 1/100$. Substituting into the above equation, we find

$$\log [H^+]_2 = -(E_{1,\,2}/0{\cdot}058 + 2),$$

from which relation $[H^+]_2$ can be readily determined. Assuming now that the sodium hydroxide in solution 2 is likewise completely ionized, its hydroxyl ion concentration $[(OH)^-]_2 =$ N/100, and hence the ionic product of water is found by the relation $K_w = (1/100)[H^+]_2$, a value close to 10^{-14} being obtained.

Very similar to the above is the determination of the solu-

bility product of AgCl from E.M.F. measurements. In this case a galvanic combination may be constructed in which half-cell No. 1 contains a silver electrode in an N/100 solution of $AgNO_3$, and half-cell No. 2 a similar silver electrode in N/10 KCl solution saturated with AgCl. This is obtained by adding to the KCl solution a small drop of dilute $AgNO_3$ solution. The two half-cells are connected by a saturated NH_4NO_3 bridge. From the E.M.F. of this combination the concentration of the Ag^+ ion in the KCl solution is calculated on similar assumptions as made above for the hydrogen ion. The concentration of the Cl^- ion in the KCl solution is known (N/10) if we assume complete dissociation. Thus the solubility product K_{AgCl} is obtained, and from it $\sqrt{K_{AgCl}}$, which is the solubility of each ion when their concentrations are equal, i.e. the solubility of AgCl in pure water. A value of about $1{\cdot}2 \times 10^{-5}$ mols per litre is obtained.

Calculation of an Equilibrium Constant from Two Standard Electrode Potentials. Reduction-Oxidation Affinity.

We take as an example the determination of the equilibrium constant of the reaction $2Fe^{+++} + Sn^{++} \rightleftharpoons 2Fe^{++} + Sn^{++++}$. We imagine a solution containing ferrous and ferric ions, and another containing stannous and stannic ions given. Platinum plates dipped into these solutions will assume a definite electrode potential, from which values of E_0 for the ferrous, ferric, and for the stannous, stannic electrode may be calculated. We indicate these values by $E_{0_{Fe}}$ and $E_{0_{Sn}}$. If the two solutions are mixed, stannous and ferric ions will disappear, being converted into stannic and ferrous ions. An equilibrium will be established in which the concentration of one of the reacting ions is so small that a direct determination of the equilibrium constant would be impossible. Such an equilibrium constant may be determined potentiometrically. This constant is defined by the equation

$$K = \frac{[Fe^{++}]^2[Sn^{++++}]}{[Fe^{+++}]^2[Sn^{++}]}, \qquad . \; . \; (12)$$

the concentrations (activities) shown being equilibrium concentrations. Assuming room temperature, we have

$$E_{Fe} = E_{0Fe} + 0{\cdot}058 \log \frac{[Fe^{+++}]}{[Fe^{++}]} \quad . \quad . \quad (6e)$$

and

$$E_{Sn} = E_{0Sn} + 0{\cdot}029 \log \frac{[Sn^{++++}]}{[Sn^{++}]}. \quad . \quad . \quad (6f)$$

In the solution in which all four types of ions are in equilibrium, $E_{Fe} = E_{Sn}$, so that we have

$$E_{0Fe} + 0{\cdot}058 \log \frac{[Fe^{+++}]}{[Fe^{++}]} = E_{0Sn} + 0{\cdot}029 \log \frac{[Sn^{++++}]}{[Sn^{++}]},$$

and hence

$$E_{0Fe} - E_{0Sn} = 0{\cdot}029 \log \frac{[Sn^{++++}]\,[Fe^{++}]^2}{[Sn^{++}]\,[Fe^{+++}]^2} = 0{\cdot}029 \log K. \quad (13)$$

By means of this equation K can obviously be calculated from the known values $E_{0Fe} = 0{\cdot}714$ volt and $E_{0Sn} = 0{\cdot}138$ volt. The result $K = 7 \times 10^{19}$ is obtained. Other equilibrium constants which are not accessible to direct measurement may be calculated in a similar manner.

Equation (13) may be generalized as follows. Two electrode reactions 1, 2 are given, of which the standard potentials are E_{0I} and E_{0II} and the factors of F are n_1 and n_2 respectively. If K denotes the equilibrium constant of a chemical reaction expressing the conversion of oxidants I plus reductants II into reductants I plus oxidants II, the coefficients having been obtained by multiplying those of electrode reaction I by n_2 and those of electrode reaction II by n_1, then

$$E_{0I} - E_{0II} = \frac{RT}{n_1 n_2 F} \ln K.$$

In the reduction of ferric by stannous ion the equilibrium constant has a very large value, which is expressed chemically by stating that Sn^{++} is a more powerful reducing agent than

Fe^{++}, and electrochemically by stating that $E_{0_{Sn}}$ is more negative than $E_{0_{Fe}}$.

Quite generally by equation (2), p. 79,

$$E_0 = -\frac{A_0}{nF}, \qquad (2a)$$

where A_0 is the standard affinity of a reductant $\rightarrow$ oxidant electrode reaction such as one of those expressed by equations (*C*9) to (*C*14) on page 75. From equation (2*a*) it is seen that the greater the affinity of a reductant $\rightarrow$ oxidant reaction the more negative is the standard electrode potential E_0 and vice versa for the oxidant $\rightleftharpoons$ reductant reaction. In equation (2*a*) E_0 is defined as the absolute value of the potential difference between the electrode and the electrolyte, which differs from measured values by an unknown constant. This constant does not, however, affect the argument. In agreement with what has been stated an " electropositive " or base metal of strong reducing power such as zinc in contact with a molar solution of its ions has a greater tendency to discharge positive ions into the solution, and assume a negative charge, than would a more electronegative or noble metal such as copper, thus giving the potential E_0 a more negative value for the more electropositive metal. This fact has already been discussed on pages 73 and 74.

In order that we may be able to state an absolute value for the affinity of an electrode reaction, it must be coupled with another. Thus if we combine a normal ferrous-ferric electrode with a normal hydrogen electrode, we find for the P.D. between the first named and the second a value of about $+0{\cdot}75$ volt. Considering the $2Fe^{++} + 2H^+$ to be the reactants, the chemical process is expressed by

$$2Fe^{++} + 2H^+ \rightarrow 2Fe^{+++} + H_2,$$

and by equation (2*a*) given above, the affinity of the process is negative, i.e. the process tends to proceed in the opposite direction to that indicated by the arrow in the equation just given.

In the example we have considered we have postulated a normal hydrogen electrode, and the affinity we have discussed is that of the reduction by ferrous ion of hydrogen ion of normal concentration to hydrogen gas of atmospheric pressure. The concentrations envisaged for the ferrous and the ferric ion were normal. Frequently an indication of the affinity of an oxidation-reduction (redox) system is given by stating the pressure of hydrogen or of oxygen that would be in thermodynamic equilibrium with the system. In the instance considered the equilibrium pressure of hydrogen can be readily found by calculating the pressure $[H_2]$ of a hydrogen half-cell of the same p_H as the ferrous-ferric cell which, when combined with it would give a chain of zero potential-difference. The required pressure $[H_2]$ is found by equating the E values of the hydrogen and the ferrous-ferric electrodes of equations (6*c*) and (6*e*), of page 80, substituting $E_0 = 0$ for the hydrogen electrode, $E_0 = 0{\cdot}75$ volt for the ferrous-ferric electrode, making $[H^+]$ of the hydrogen electrode equal to the hydrion concentration of the ferrous-ferric electrode and $[Fe^{+++}] = [Fe^{++}] = 1$. The value obtained is so small as to be of only indirect physical interest. In order to obtain convenient numbers W. Mansfield Clark at one time advocated the introduction of a constant r_H which in analogy to p_H is defined by the equation $r_H = -\log[H_2]$.

The equilibrium pressure of oxygen $[O_2]$, with a system for which the hydrogen equilibrium pressure at ordinary temperature is known, may be found by means of the thermodynamically derivable relation: $[H_2]^2[O_2] = 10^{-86}$ (atmospheres)^3.

Oxidation-Reduction Indicators.

In recent years indicators such as methylene blue known as oxidation-reduction indicators have been used to measure the oxidation-reduction " balance " or " intensity " of solutions. In the case of methylene blue we have a dyestuff that is capable of reversible reduction to a colourless leuco compound. In other cases the oxidized form has one colour, the

reduced form another. In general we meet with a relation which is quite analogous to that existing between the acid and the alkaline forms of the indicators discussed on p. 37. We shall refer to the oxidized form of the indicator by Ox, the reduced form by Re, so that the conversion of one form into the other is expressed generally by the chemical equation

$$\mathrm{Ox} + n\mathrm{H} \rightleftharpoons \mathrm{Re}.$$

If a plate of a metal such as platinum is immersed in a solution containing the indicator, we may consider the surface of the plate capable of establishing within it an equilibrium concentration of hydrogen, and thus a definite electrode potential by the interaction of hydrogen ions of the solution with electrons in the plate according to the equation $\mathrm{H^+} + \epsilon \rightleftharpoons \mathrm{H}$. Writing therefore for H, $\mathrm{H^+} + \epsilon$, we have:

$$\mathrm{Ox} + n\mathrm{H^+} + n\epsilon \rightleftharpoons \mathrm{Re},$$

or, expressed for the reaction in bulk:

$$\mathrm{Re} + nF \rightleftharpoons \mathrm{Ox} + n\mathrm{H^+}. \qquad (C16a)$$

According to equations (*C*15) and (4) (pp. 76 and 79), the electrode potential is given by:

$$E_h = E_0 + \frac{RT}{nF} \ln \frac{[\mathrm{H^+}]^n[\mathrm{Ox}]}{[\mathrm{Re}]}. \qquad (14)$$

Transposing and expressing in volts for 30° C., we have:

$$E_h = E_0 \quad 0{\cdot}060p_{\mathrm{H}} + \frac{0{\cdot}060}{n} \log \frac{[\mathrm{Ox}]}{[\mathrm{Re}]} \text{ volt}. \qquad (14a)$$

E_0 is known as the standard " oxidation-reduction " or standard " redox " potential of the indicator.

If we introduce an oxidation-reduction indicator in small concentration into a solution of high concentration, which is itself an oxidation-reduction or " redox " system, and which we shall refer to as the test system, equilibrium between the indicator and the test systems will be established, E_h becoming

the same for both systems at practically the E_h value of the more concentrated test system. This will lead to an adjustment of the [Ox] to [Re] ratio of the indicator according to equations (14), and at E_h values not far removed from the one at which [Ox] = [Re] a change in colour will be produced just as in the analogous case of the Ac to Alk equilibrium considered on p. 38.

It will be seen from equations (14) and (14*a*) that an oxidation-reduction indicator is characterized by its constant E_0, which may be defined as the value of E_h in a solution in which the hydrion concentration is normal ($p_H = 0$) and the ratio [Ox] : [Re] = 1. Usually, however, oxidation-reduction indicators are described by means of a quantity E_0', which is defined by the equation $E_0' = E_0 - 0{\cdot}060p_H$ (for 30° C.). Values of E_0' are usually quoted for $p_H = 7$. To determine these experimentally E_h is measured in a solution of p_H close to 7, the ratio [Ox] : [Re] being determined by one of the visual methods discussed on p. 39 *seq.*

The Quinhydrone and Similar Oxidation-Reduction Electrodes.

It follows from equations (14) and (14*a*) that the electrode potential of an oxidation-reduction indicator, whose [Ox] to [Re] ratio is not interfered with by a second oxidation-reduction system, varies with p_H in exactly the same way as does the potential of a hydrogen electrode, and that it may therefore be used to measure p_H. For this purpose it is of course unnecessary that either the oxidant or the reductant form should be coloured. A very important electrode of the oxidation-reduction type, due to E. Biilmann (1920), is the quinhydrone electrode. Quinhydrone, being a compound of equimolecular quantities of quinone and hydroquinone, behaves in solution as a mixture of these. A constant ratio of [Ox] to [Re] is thus obtained irrespective of the concentration of the quinhydrone. Electrodes in which either the oxidant or the reductant form or both forms are at saturation concentration are exemplified by the quinoquinhydrone electrode in which quinhydrone and quinone, the hydroquinhydrone

electrode in which quinhydrone and hydroquinone, and the chloranil electrode in which chloranil (tetrachloroquinone) are used at saturation concentration.

If we substitute in equation (14) the appropriate values for the constants, and combine them all into one new constant E_0'', characteristic of the oxidation-reduction electrode under consideration, we have:

$$E = E_0'' - 0{\cdot}000198 T p_{\mathrm{H}} \text{ volt.} \qquad (14b)$$

The constant E_0'' has the following values at ordinary temperature, the normal hydrogen electrode being the reference electrode:

for the quinhydrone electrode, $E_0'' = 0{\cdot}704$ volt;
for the quinoquinhydrone electrode, $E_0'' = 0{\cdot}756$ volt;
for the hydroquinhydrone electrode, $E_0'' = 0{\cdot}618$ volt;
and for the chloranil electrode, $E_0'' = 0{\cdot}669$ volt.

CHAPTER VII

IRREVERSIBLE ELECTROLYTIC PROCESSES. POLARIZATION. STRUCTURE OF ELECTROLYTIC DEPOSITS

Concentration Changes

(*a*) *A Stationary Electrolyte.*

When a current passes from an electrolyte to an electrode, ions are removed from the electrode layer, i.e. the layer of electrolyte immediately adjacent to the electrode, and discharged as atoms. Thus, when copper is deposited on an electrode from a neutral sulphate solution by means of a current density I units per unit area, the amount deposited per unit of area and time is I/F gram-equivalents. Of this $T_k I/F$ is replaced by migration, the remainder,

$$\phi = T_a I/F, \tag{1}$$

is removed. T_k and T_a are the transport numbers of the cation and anion, equations (3*a*) and (3*b*) (p. 11). This deficiency is made good by diffusion; if it were not so, the ionic concentration in the electrode layer would instantly sink to zero, and the passage of the current would stop. We may thus talk of a flow ϕ of ions by diffusion towards the electrode. This flow, as was discovered by Fick in 1855, is nearly proportional to the concentration gradient, being almost independent of the concentration. We may therefore write

$$-D\frac{\partial C}{\partial l}, \tag{2}$$

D being the diffusion coefficient of the electrolyte and l a length co-ordinate. For linear diffusion we also have: *

$$\frac{\partial \phi}{\partial l} \qquad \frac{\partial C}{\partial t}.$$

Liquid diffusion is thus subject to the same mathematical treatment as that elaborated by Fourier at the beginning of the nineteenth century for the conduction of heat in a solid.

The simplest case is that of diffusion in an infinite straight line. This case is realized by a cylindrical vessel filled with electrolyte, and closed at the top by a flat horizontal cathode, on which a metal such as copper is being deposited by a uniform current of density I. The " flow " of ions ϕ across the electrode layer is given for a neutral copper sulphate solution by equation (1). This flow may be considered as made up of infinitely many pulses $\phi\, dt$, each lasting for the differential of time dt. Mathematical analysis shows that each of these pulses will produce a concentration change dC at the distance l from the electrode after the time t, which is independent of the original concentration and of the other pulses, and is given by the equation: †

$$dC = -\frac{\phi}{\sqrt{\pi D t}} e^{-(l^2/4Dt)}\, dt.$$

Application of this result to the case considered above of a neutral copper sulphate solution of original equivalent concentration C_0 leads to the following result for the concentration at any point in the liquid:

$$C = C_0 - \frac{T_a I}{F\sqrt{\pi D}} \int_0^t \frac{1}{\sqrt{t}} e^{-(l^2/4Dt)}\, dt, \qquad (3)$$

* For imagine in fig. 1, p. 9, a portion of the solution of unit sectional area between the two parallel planes shown, then the increase of solute in this portion in the time ∂t is equal to $-\partial\phi\, \partial t$ and also to $\partial l\, \partial C$.

† A compendium of mathematical results arising out of the theory of diffusion will be found in Kelvin's *Collected Papers*, Vol. II, p. 46. A deduction of equation (3) by integration of the fundamental differential equation under the conditions of the problem is given by the writer in *Phil. Mag.*, 1901, p. 45.

and for the electrode layer ($l = 0$) to:

$$C = C_0 - \frac{2T_a I}{F\sqrt{\pi D}}\sqrt{t}. \qquad . \; . \; (4)$$

Making $C = 0$ in this expression, and transposing, we find for which elapses, until the concentration in the electrode layer becomes zero:

$$t_0 = \frac{\pi D F^2 C_0}{4T_a^2 I^2} \qquad (4a)$$

It will be seen that this time is directly proportional to the square of the original concentration, and inversely to the square of the current density, a result that has been experimentally verified. The application of this equation also enabled the writer to conclude from his experiments (*Phil. Mag.*, loc. cit.) that hydrogen is only liberated from a copper sulphate solution after the concentration of the copper ions in the electrode layer has gone down to zero.

It was also shown that equation (63*b*) applies not only to neutral copper sulphate solutions, but also with considerable approximation to copper sulphate solutions containing sulphuric acid, if making $T_a = 1 - T_k$, we attach to T_k the significance given to it in the general definition of p. 10.

It must not be forgotten that the results given apply only to linear diffusion in the absence of all convection. Where diffusion proceeds from more than one direction in space, the result is of a different nature. Thus, when diffusion takes place from all directions to the surface of a small sphere of radius r, the concentration in the electrode layer does not go down indefinitely with time, but approaches a limiting value, which is given by the equation:

$$C = C_0 - r\frac{IT_a}{FD}. \qquad . \; . \; . \; (5)$$

(*Trans. Chem. Soc.*, 1910, **97**, 922.)

(*b*) *A Vigorously Stirred Electrolyte.*

In contrast to the conditions just discussed of a stationary electrolyte, Nernst and Brunner considered the case of a vigorously stirred electrolyte (*Zeit. Phys. Chem.*, 1904, **47**, 52 and 56). They assume that the electrode layer adheres sufficiently to the electrode to avoid slipping, but that at a definite distance δ from the electrode, which is termed the thickness of the diffusion layer, and which depends on the vigour of stirring and on the viscosity of the solution, its average concentration is maintained. In the diffusion layer a permanent condition is soon established, in which the flow of ions entering the layer is the same as that leaving it.

We consider the cathodic process in a stirred electrolyte which contains a small amount of a depolarizer, for example that taking place in a solution of sulphuric acid to which a small amount of silver sulphate has been added. In the diffusion layer the current will be carried mainly by the ions of the sulphuric acid, and we propose to neglect the transfer of electricity in the layer by the silver ions. The transfer of current from the solution to the cathode will, however, take place exclusively by the discharge of silver ions, so long as these have an appreciable concentration. Indicating their equivalent concentration in immediate contact with the cathode by C_0, their concentration outside the diffusion layer by C, the thickness of the latter by δ, the flow of silver ions by diffusion by ϕ, the current density by I, and the diffusion coefficient of the silver ions, which is calculated from their mobility by equations (9*a*), p. 87, and (6*a*), p. 20, by D, we have in the permanent condition:

$$\phi = \frac{I}{F} = D\frac{C - C_0}{\delta}. \qquad \ldots \quad (6)$$

The maximum value for the flow of silver ions due to diffusion, ϕ_0, and the corresponding current density I_0, carried

across the electrolyte-cathode boundary exclusively by the discharge of silver ions, are thus given by:

$$\phi_0 = \frac{I_0}{F} = D\frac{C}{\delta}. \qquad (6a)$$

The value of I_0, which may be termed the current density limit, can be determined experimentally, for any increase above it involves the simultaneous evolution of hydrogen, and therefore a large change of electrode potential, which can be readily detected. The quantities occurring in equation (6*a*) are thus all known with the exception of δ, which can therefore be determined from the equation. Instead of an ion any depolarizer of known diffusion coefficient may be employed. The values for δ found by Brunner varied from about 0·02 to 0·05 mm.

Polarization, Deposition or Decomposition Potentials, Overpotentials.

We imagine that a constant current is being passed through a galvanic cell, and that the potential difference between its electrodes is being measured. In most cases it will be found that the potential difference changes in such a manner as to oppose the current. We now imagine the latter interrupted, and the electrodes connected by a wire. Then, if the cell is symmetrical, i.e. if it is built up of two like electrodes in a common electrolyte, a current will usually be found to flow in the opposite direction to the original impressed current. The phenomenon of change of potential between the electrodes is termed quite generally **polarization,** and the current obtained on disconnecting and shortcircuiting, a **polarization current.** A cell that shows no polarization is a **reversible cell.** Polarization may be due to an obvious change in the character of the cell. Thus if zinc is deposited on a platinum electrode from a zinc sulphate solution, the character of the electrode is obviously changed. Such polarization we shall not consider. Polarization may also be produced by changes of concentration such as we have discussed.

This polarization is known as **concentration polarization,** and the possibility of its occurrence must never be lost sight of. Hindrances to the passage of a current may also be produced by the formation of badly conducting or almost non-conducting films on electrodes. Instances of this kind are the films of alumina which may form on aluminium anodes, and also anodic films which produce "passivation" on metals such as iron and chromium. Such films will, however, produce only momentary polarization currents due to condenser effects, and hence they are usually not considered to be the cause of true polarization.

To obtain a clear view of what is taking place in a cell during the passage of a current, it is necessary to study each electrode separately. The methods available for this purpose we shall describe in the sequel. The potential differences measured should always be referred to some clearly defined standard electrode. They are termed **deposition** or **decomposition potentials.** In many cases of electrolytic action such as the liberation of hydrogen or of a metal from an aqueous solution, it is possible to envisage an electrode at which the electrolytic process under consideration would take place "reversibly". The absolute value of the difference of potential between the electrode under investigation and its reversible or equilibrium potential as just defined is known as the **overpotential** or **overvoltage** of the electrode. By conception overpotential is a polarization, and should therefore normally have a positive value. It is therefore usually defined as the difference between equilibrium and deposition potential in the case of cathodic, and as the difference between deposition and equilibrium potential in the case of anodic polarization. Some writers, however, define overpotential in all cases as the difference between deposition and equilibrium potential. It is then normally negative for cathodic and positive for anodic polarization.

A **depolarizer** is a substance which substitutes for the reaction taking place at an electrode, another reaction proceeding with less hindrance to the passage of the current. Thus reducing substances act as depolarizers in anodic,

oxidizers as depolarizers in cathodic processes. Depolarizers may give to overpotential as usually defined an *apparently* negative sign.

Measurement of Deposition Potential at Single Electrodes

(*a*) *Measurement during the passage of the Current.*

The measurement of deposition potential during the passage of a current differs from that of equilibrium potential in the fact that arrangements must usually be made to tap off a liquid connexion to the standard electrode as nearly outside the lines of flow of the current as possible. If this is neglected, potential differences due to the ohmic resistance of the electrolyte will be included in the results of measurement. The fact that all electrolytic potential measurements contain an unknown constant due to the standard electrode has been repeatedly referred to. The best-known method for tapping off the liquid connexion is probably that due to Luggin and Haber. It consists in the employment of a thin glass capillary containing the junction liquid. Haber employed capillaries little more than a tenth of a millimetre in thickness, which were elastic enough to allow them to be laid flat against the working electrode. Another device consists in the adoption of a working electrode which forms part of the casing of the electrolytic vessel, so that current cannot flow behind it. Into the electrode a fine hole is pierced, behind which a liquid connexion to the auxiliary electrode is tapped off. Akin to this is the method which is usually adopted in electrolytic analysis. A gauze cylindrical working electrode is employed, in the interior of which the other electrode is placed, so that the whole of the current is confined to the space between the two electrodes. A liquid connexion may then be tapped off anywhere outside the working electrode.

In a technique which belongs to a different class from those hitherto considered, and which was used extensively by Nernst for measuring the dependence of current on applied E.M.F.,

the potential difference between anode and cathode may be measured directly without the intervention of an auxiliary electrode. This is rendered possible by making the electrode under observation, which we shall term the " working " electrode, very small, the other one being relatively large. By this device the polarization of the large electrode is made practically stationary, owing to the smallness of the total current required, and the potential difference needed to overcome the ohmic resistance of the electrolyte remains negligible for the same reason. A modification of this method is that due to Kučeras and Heyrovský, in which both electrodes are of mercury. This technique has the advantage of keeping the surface of the working electrode fresh by allowing the mercury to drop in a continuous stream through a fine capillary.

(*b*) *Measurement of Deposition Potential during momentary interruption of the Current.*

Another method of determining deposition potential consists in interrupting the current momentarily, and measuring the electrode potential during the interval. The need to tap off the connexion to the standard electrode from the immediate vicinity of the working electrode thus disappears. In the older researches interruption of the current was made by a tuning-fork, which connected the working electrode alternately to the battery circuit and to the auxiliary electrode measuring circuit. In more recent times Newbery and others have employed rotary commutators for the same purpose. Measurements made during interruption of the current are therefore commonly referred to as made by the *commutator method*, in contrast to those made during the passage of the current, which are described as made by the *direct method*. It might be thought that measurements made by the commutator method would in all cases yield results entirely different from those obtained by the direct method. This is, however, not the case. For low current densities both methods lead to substantially the same results, as was shown for example by

W. V. Lloyd's experiments on the liberation of hydrogen on bismuth and antimony cathodes (*Trans. Faraday Soc.*, 1929, **25**, 528). The reason for this may be sought in the fact that, whatever the principles of measurement, it is primarily the products of electrolysis that are responsible for polarization. Even in cases where polarization is produced by badly conducting films, through the pores of which the current passes, the films will behave as condensers, and the two methods yield nearly the same results. The polarization that is due to solid films and to gases usually decays with great rapidity. In the experiments on overpotential carried out by Sand, Grant and Lloyd (*J. Chem. Soc.*, 1927, p. 378) a rotary commutator was employed, which made connexion to the measuring circuit during intervals of only $2{\cdot}2 \times 10^{-4}$ seconds after breaking the current. Even shorter periods of interruption have been attained recently by A. Hickling by means of an ingenious valve circuit free from moving parts (*Trans. Faraday Soc.*, 1937, **33**, 1540). Newbery employed the cathode ray oscillograph to obtain the decay curves of polarization. For a given electrolytic process measurements of deposition potential, made by the commutator method at high current densities of, say, more than 10 milliamperes per square centimetre, tend to assume a constant value independent of the current density. On the other hand, deposition potentials measured by the direct method increase indefinitely with current density, and appear to contain a term which is due to the passage of the current through an almost constant resistance on or near the surface of the cathode. The existence of an ohmic " transfer " resistance at higher current densities is in agreement with results obtained by Newbery by means of the cathode ray oscillograph. According to this worker, it is due to a very thin gas film (*Proc. Roy. Soc.*, 1928, A, **119**, 686).

When interrupted current is used, the current strength is defined as the number of coulombs that cross the electrode per second. This is measured by the reading of an ordinary dead-beat ammeter and is smaller than the current strength during the intervals when the current is on.

Results of Overpotential Measurement.

Metal Overpotentials.—As already stated, overpotential during the deposition of metals such as silver, mercury, copper, bismuth, lead, and zinc from solutions of their simple ions is usually small, and seldom exceeds four or five centivolts. Very much higher values up to about one volt may be obtained when these same metals are deposited from their cyanide solutions, or from other complex compounds. According to Glasstone (*J. Chem. Soc.*, 1929, pp. 690, 702), we are in the case of argenti and cuprocyanides dealing largely with concentration polarization. As discovered by Foerster and Coffetti in 1905, "metal" overpotentials of a larger order than with other metals, and amounting to about 0·15 volt, are found when iron, nickel, and cobalt are deposited from solutions of their simple ions with current densities of about one milliampere per square centimetre at ordinary temperature. These overvoltages increase with higher current density, they decrease at higher temperature, and practically disappear at boiling temperature, a fact which is of considerable importance in certain metal separations. In these cases the freshly deposited metals are found to contain hydrogen, and the metals also show abnormalities with regard to their equilibrium potentials, inasmuch as these are greatly influenced by the presence of hydrogen or oxygen. Metals deposited from solutions containing colloids may also show considerable overpotential when these colloids are co-deposited with the metal.

Gas Overpotentials.—Gas overpotentials are found to be extremely variable according to the conditions under which the gas is liberated. We have already seen that the over-potential of hydrogen on a platinized platinum electrode is practically zero at moderate current densities. The same holds for a palladium sponge electrode. Overpotentials sufficient to produce a visible evolution of hydrogen were first determined in 1884 by Pirani on Helmholtz's suggestion (*Wied. Ann.*, 1884, **21**, 68), and later more comprehensively by Caspari (*Zeit. Phys. Chem.*, 1899, **30**, 89). On a polished platinum

electrode visible evolution of hydrogen requires a minimum overpotential of about eight centivolts. On a cathode of polished nickel about 0·3 volt, on copper about 0·4 volt, on cadmium and silver about 0·5 volt, on zinc about 0·7 volt, and on lead and mercury 0·8 volt are necessary. When these same metals are in a spongy condition, very much smaller overpotentials are found; thus a cathode of spongy copper requires an overpotential nearly 0·3 volt less than one made from the polished metal. According to researches carried out by J. Tafel in 1905 (*Zeit. Phys. Chem.*, 1905, **50**, 668), overpotential increases proportionally to the logarithm of the current density for certain ranges of the latter. This result has been confirmed by many investigators. The general form of the relation found is given on p. 115. Gas overpotentials decrease considerably with temperature.

As regards the effect of hydrogen ion concentration on overpotential, Herasymenko (*Rec. Trav. chim. Pays-Bas*, 1925, **46**, 503), using the dropping mercury electrode, arrived at the conclusion that hydrogen overpotential increases by 0·058 volt at ordinary temperature when the hydrogen ion concentration is decreased to one-tenth. F. P. Bowden (*Trans. Faraday Soc.*, 1928, **24**, 473) arrived at a similar conclusion, but only when the larger currents were employed. It is not quite certain whether concentration polarization influenced these results or not. Apparently extremely high overvoltages are obtained when neutral solutions are electrolyzed. These are no doubt spurious, since in such solutions electrolysis at once makes the electrode layer alkaline, and thus produces a large change in p_H. This change causes a considerable concentration polarization which is indistinguishable from overpotential. Hydrogen overpotentials in alkaline are of the same order as in acid solution. Here sodium or potassium alloys may be formed, which may disintegrate more or less explosively. Thus clouds of finely divided metal are formed when cathodes of lead, tin or bismuth are employed at high current densities in alkaline solution, and considerable pitting of the electrodes takes place (Haber and Bredig, *Ber.*, 1898, p. 2741). When mercury cathodes are employed, sodium

amalgam is formed, as is familiar from the application of this fact in the Castner Kellner process of alkali manufacture.

The electrolytic evolution of oxygen is always accompanied by considerable overpotential, and it is therefore not possible to obtain reversible oxygen electrodes. Intermediate oxides are believed to play a part even with such metals as platinum and gold, and to the formation of these the fact is ascribed that oxygen overpotential tends to increase with time. It is apparent that any change on the surface of the electrode will show itself in a change of overpotential, and we thus frequently meet with drifts of overpotential with time both for anodes and for cathodes. Oxygen overpotential appears to be increased by the presence of fluorides; it is usually decreased by oxygen carriers such as manganese, cerium, or vanadium compounds.

Causes of Overpotential.

No complete explanation exists for the metal overpotential of iron, nickel, and cobalt. Though, as stated above, it is known that these metals are deposited alloyed with hydrogen, it is not apparent why the pure metal with a smaller free energy should not be formed in preference to the alloy having a higher free energy. All that can be said is that the phenomenon of a metastable form arising in preference to a stable one, that is, a form of high free energy content being produced in preference to one of lower free energy, is not uncommon.

With hydrogen, oxygen, and other gases it is, however, chemically apparent that the passage from the ionized to the unionized state will lead in the first instance to the formation of atoms. In the case of hydrogen, for example, we must assume that the kinetics of the discharge process are represented by $H^+ + \varepsilon = H$. The bi-ionic process, $2H^+ + 2\varepsilon = H_2$, appears to be ruled out on account of the mutual repulsion of the charges on the ions. Now free atomic hydrogen has a very much greater free energy content than the same substance in the molecular form. Thus the total dissociation energy of 2 gm. of molecular into atomic hydrogen is known

to be about 100,000 calories, and we may assume the free energy change to be of a similar order. From this we calculate that gaseous atomic hydrogen of atmospheric pressure, or its saturated solution in the electrolyte, would require more than 2 volts in excess of the equilibrium potential of molecular hydrogen for its production. At overpotentials very considerably smaller than 2 volts, such as those actually encountered, gaseous monatomic hydrogen can only be present in vanishingly small concentrations. It is, however, in the compound electrode layer, consisting of the electrode surface and of molecules and ions in the liquid phase in immediate contact with it, that chemical reaction resulting in the production of molecular hydrogen takes place, and it is this layer that we must consider. Owing to catalytic influences, hydrogen atoms may very well be adsorbed on the surface and to some extent be held in the interior layers of the metal electrode in sufficient concentration to allow encounters between two hydrogen atoms to take place here with great frequency. For chemical reasons such encounters may be assumed to lead practically invariably to the production of molecules. We thus see that overpotential will be determined by the assistance given by the atoms of the electrode in promoting encounters between atoms of hydrogen, and we have a ready explanation of the selective influence of different metals on hydrogen overpotential. The experimental fact is quite in agreement with this, that those metals which have the strongest adsorption affinity for hydrogen should depress overpotential most, and that they should generally be catalytically the most active in hydrogen reactions. For a given metal, provided that the arrangement of its atoms in the surface layer is not liable to variation, a given overpotential for a given current strength should correspond to the same true surface area, a consideration which is the basis of an ingenious suggestion by Bowden and Rideal for the measurement of true surface area (*Proc. Roy. Soc.*, A, 1928, **120**, 59).

In the case of catalytically inactive metals such as mercury, the surface concentration of adsorbed hydrogen atoms, even under the influence of high overpotentials, is probably so

small that encounters between individual atoms practically do not occur. The writer has suggested that in this case the complex ion H_2^+, consisting of two protons held together by one electron, may play a part in promoting the formation of hydrogen molecules and thus in determining overpotential (*Trans. Faraday Soc.*, 1929, **26**, 19). This suggestion has later been adopted by others (J. Heyrovský, *Coll. Czech. Chem. Comm.*, 1937, **9**, 282). It is envisaged that although encounters between hydrogen atoms play no measureable part in the production of molecules, yet collisions with the relatively abundant hydrogen ions lead to the formation of H_2^+ ions at a rate sufficient to carry the current. At low current densities it may be supposed that the hydrogen atoms are held in extremely minute surface concentration by the mercury, and that the rate of formation of H_2^+ ions is proportional to the number of impacts of hydrogen ions against the electrode. At higher current densities the mercury surface may be supposed to become saturated with hydrogen atoms. Further hydrogen atoms are therefore discharged into the liquid in the immediate vicinity of the electrode, where they interact with hydrogen ions. The H_2^+ ions are supposed to be instantly discharged on formation, so that they assume no measurable concentration. Conclusions drawn from these assumptions are in general agreement with experimental results.

In cases in which chemical hindrances are completely eliminated by catalytically active electrodes, there is still the possibility of the well-known physical hindrance making itself felt, which opposes the production of small bubbles of gas for reasons of surface tension, and is the cause of the superheating of liquids at their boiling-point. Thus Helmholtz in 1882 electrolyzed boiled out dilute sulphuric acid between platinum electrodes. He found that to produce an initial current a perceptible overpotential was required, which disappeared after the current had set in, just as a liquid is heated above its boiling-point before ebullition begins. Similarly, Marie showed in 1908 that substances like gelatine, which promote the superheating of liquids, also favour over-

potential. Overpotentials clearly traceable to hindrances in the formation of gas bubbles are much smaller than those due to chemical causes, and should be practically absent from electrodes on which rapid evolution of gas is taking place. We may calculate that if water were superheated at atmospheric pressure to 105° C., the free energy of the liberated steam bubbles would amount to about 553 joules per mol. If as an upper limit we assume that electrolytic hydrogen acquires this same free energy per mol before it is liberated as bubbles, the excess potential would amount to $553/2F$ or 0·00286 volt, which is of a much smaller order of magnitude than overpotentials commonly observed. Quantitative results on the variation of overpotential with bubble size were obtained by MacInnes and Adler (*J. Amer. C. S.*, 1919, **41**, 194), and MacInnes and Conterri (*J. Amer. C. S.*, 1919, **41**, 2013).

J. A. V. Butler (*Phil. Mag.*, 1924, **48**, 927), and R. W. Gurney (*Proc. Roy. Soc.*, 1931, A, **134**, 137) have considered the process of ion discharge in the light of modern ideas of quantum mechanics. Gurney arrived at a result, which is in qualitative agreement with F. P. Bowden's observations on the variation of overvoltage with current density and with temperature (*Proc. Roy. Soc.*, 1929, A, **125**, 446; **126**, 107). It is claimed that the theory provides a comprehensive explanation of overpotential. As such it appears to the writer to suffer from over-simplification. For an exposition of quantum mechanical principles the reader is referred to R. W. Gurney's " Elementary Quantum Mechanics ", Cambridge, 1934.

Practical Importance of Overpotential.

The importance of overpotential as a means to produce hydrogen of high free energy content was first recognized by J. Tafel. In a series of researches beginning about 1900, he showed that to reduce substances electrolytically, which offer much resistance to reduction, such as caffein and other derivatives of xanthine and uric acid, and ketones and oximes in general, it is necessary to employ mercury or lead cathodes,

which have a high hydrogen overpotential. Similar cathodes must be employed for the reduction of arsenic acid to arsine (Sand and Hackford, *Trans. Chem. Soc.*, 1904, **85**, 1018). Though of very great importance in electrolytic reduction, the free energy content of the hydrogen, which is determined by overpotential, is not the only governing factor. The catalytic effect of the metal is also of importance. Thus cathodes of spongy copper, on which there is only a very small hydrogen overvoltage, are particularly effective in the reduction of nitrobenzene to aniline.

The possibility of depositing metals such as tin, lead, cadmium, and zinc, which are baser than hydrogen, from acid solution rests on hydrogen overpotential. In all such depositions success depends on excluding impurities which might deposit on the cathode, and lower its overpotential.

The importance of overpotential in determining the relative rates of two simultaneous electrolytic processes is discussed in a subsequent section. Thus the preferential liberation of light, as compared with heavy, hydrogen from a solution containing both hydrogen and deuterium ions is due mainly to the greater overpotential of deuterium, and the equilibrium potentials would not furnish a satisfactory basis of separation (J. Heyrovský, *loc. cit.*). According to an experimental investigation by C. Drucker, (*Trans. Faraday Soc.*, 1937, **33**, 660) the E_0 value for the equilibrium of hydrogen with its ions (solution tension of hydrogen) is the same as the corresponding quantity for deuterium. This leads to the conclusion that the limit of separation which could be based on equilibrium potentials alone is represented by an equimolecular concentration of hydrogen and deuterium ions.

Consecutive Electrolytic Processes.

To fix our ideas on a specific case, we consider an acidified solution, containing the ions of silver, copper, cadmium and zinc, in which a pair of platinum electrodes has been placed. The equilibrium potentials E_h of the metals chosen, with solutions of their ions at molar concentration are given respectively as $E_0 = +0{\cdot}80$, $+0{\cdot}34$, $-0{\cdot}40$, and $-0{\cdot}76$ volt.

We imagine an increasing potential difference to be impressed on the pair of electrodes, until silver begins to deposit. Let us suppose that the solution is at ordinary temperature and that its concentration in the vicinity of the electrode layer is 1/100 molar. The cathode will be just slightly more negative than the equilibrium potential of silver with 1/100 molar silver ions, i.e. by equation (6*a*), p. 80, E_h will be slightly below 0·684 volt. Let us further suppose that the concentration of the copper ions is 0·1 molar and hence the equilibrium E_h value of a copper electrode at room temperature by equation (6*b*), p. 80, equal 0·31 volt. At an electrode potential of 0·684 volt copper would therefore not deposit from the solution; on the contrary, suppose that for any reason the electrode had previously a coating of metallic copper, this would go into solution, forming copper ions. Copper would only begin to deposit at a cathode potential more negative, i.e. smaller than 0·31 volt. At this potential the calculated equilibrium concentration $[Ag^+]$ of the silver ions is $[Ag^+] = 3{\cdot}5 \times 10^{-9}$ molar. If, then, the solution is kept stirred so that no appreciable difference can arise between the concentration of the silver ions near the electrode layer and the bulk of the solution, it is quite possible to extract practically the whole of the silver without any deposition of copper by maintaining the E_h value of the cathode above 0·31 volt, and so to effect a complete separation of the two metals. The E_h of the cathode may be controlled by means of the P.D. between anode and cathode; but with greater precision by the employment of an auxiliary electrode.

After the silver ions in the electrode layer have disappeared, it is possible to make the cathode more negative than corresponds to $E_h = 0{\cdot}31$ volt, and copper will be deposited. Applying the method just explained, we see that when an electrode potential of $E_h = 0$ is attained, the Cu concentration should be between 10^{-11} and 10^{-12} normal. At this concentration hydrogen ions would begin to be discharged, were it not for the overpotential of the gas. We have seen that to obtain a visible evolution of hydrogen on a copper electrode an overpotential of 0·4 volt is necessary, which

increases with increasing current density. There is thus nothing to prevent cadmium from being deposited along with hydrogen once the copper has been removed. If a separation of copper from cadmium in our solution is desired the cathode potential must be controlled, just as in the case of the separation of silver from copper. There is, however, another method by means of which the deposition of cadmium can be inhibited, viz. by the use of a depolarizer. As such, nitric acid is frequently employed, which may be reduced to nitrous acid and ammonia, before the cathode potential becomes negative enough to allow the deposition of metals such as cadmium and more particularly zinc. Thus from a solution which has been acidified with a suitable amount of nitric acid, copper may be separated from zinc without external control of the cathode potential. From a feebly acid solution in the absence of oxidizing agents cadmium may be separated from zinc, if the cathode potential is kept under control.

In the separations we have considered, metal overvoltage plays only a small part. Nevertheless, it may be taken that a separation of metals by controlled potential is not practicable, unless their normal equilibrium voltages are at least 0·3 volt apart.

Where metal overpotentials are high, as in the case of nickel, it is necessary to reduce them to a minimum, when effecting separations by working in hot, or nearly boiling, solutions.

There is another influence which affects the separation of metals, viz. the formation of solid solutions, or compounds. Thus, when solutions containing the chlorides of antimony and copper are electrolysed, a purple alloy of the two metals may be obtained. A case of compound formation that is of importance in electrolytic analysis is that of arsenic and copper. Thus it was shown by Torrance (see Vol. II) that arsenic can only be removed quantitatively from solution if copper is co-deposited with it, so that the formation of an alloy containing copper arsenide may take place. Where metal overpotential is met with, there is special scope for

alloy formation. Thus alloys of copper and zinc can be readily deposited from the mixed double cyanide solutions of these metals. A very interesting instance of alloy formation in which metal overvoltage plays a part is furnished by the deposition of nickel with iron or with zinc. When solutions containing the sulphate of nickel in addition to that of either of the other metals are electrolysed at ordinary temperature, alloys are obtained, in which the baser metal predominates, even when the nobler is present in higher concentration in the solution. Attention was first drawn to this surprising phenomenon by the experiments of H. Toepffer in 1900 (F. W. Küster, *Zeit. Elektrochem.*, 7, 257 and 888). It has since been confirmed by a number of other investigators.

A familiar case, in which alloy formation plays an important part, in reducing the negative value of deposition potential, is the liberation of sodium as a dilute amalgam in the Castner Kellner process. Another instance is the formation of nickel magnesium alloys by the electrolysis of aqueous solutions of the mixed sulphates. In each of these cases it is not possible to obtain the baser metal alone by the electrolysis of aqueous solutions, since only hydrogen would be produced. Alloy formation, however, makes the deposition of the metal possible, though even so, the rôle of overpotential in inhibiting the liberation of hydrogen must not be overlooked.

A very important factor in metal deposition is the power of metallic ions to form complexes. Cations, such as those of silver and copper, may be practically removed from solution by causing them to unite with cyanide ions to form complex anions. Other simple cations may by suitable combination form complex oxalate, sulphide or fluoride ions. In some cases complex formation may make it impossible to deposit a particular metal from an aqueous solution, in others it may cause the sequence in which metals are deposited to be reversed. Thus, in contrast to the sequence of their deposition from simple salt solution, both bismuth and cadmium are deposited before copper from alkaline solutions containing cyanide. Facts such as these can obviously be utilized in

the separation of metals for purposes of electrolytic analysis.

Simultaneous Electrolytic Processes.

In the preceding section we considered the sequence of two electrolytic processes one of which practically goes to completion before the next starts. These processes were assumed to take place with practically no overpotential, so that apart from concentration polarization the electrode potential was independent of current density. Such independence, however, though often approached in metal deposition, does not exist as a general rule. Usually the variation of electrode potential with current density must be represented by empirical curves. The researches of Haber and his co-workers carried out at the beginning of the present century, and the subsequent ones of Tafel on hydrogen overpotential, have shown that over a considerable range such curves are of the general form $E = a + b \log I$, where E and I have their usual significance, and a and b are constants depending on the process. Therefore if two reactions take place simultaneously at the same electrode at the potential E, we may ascribe to one of them the current I_1, to the other the current I_2, the total current being $I = I_1 + I_2$, and in most cases we may assume the part currents to be expressed by the equations $E = a_1 + b_1 \log I$, and $E = a_2 + b_2 \log I$, the constants of which are characteristic for each reaction. Such equations enable us to calculate the part currents and thus the share of each reaction at any given value of E. More generally, if we plot the E, I curves for each of the two reactions, we shall obtain an estimate of the share of each at a given value of E by comparing the respective I values.

Consecutive Determination of Decomposition Potentials.

To determine consecutive deposition or decomposition potentials in an electrolytic cell, a gradually increasing potential difference is applied to its poles. This may be done by means of a rheostat which is shunted across an accumulator, while the cell is connected to one end and the slider. The

applied P.D. may be read on a voltmeter, and the current passing through the cell on a galvanometer. Where a decomposition or deposition sets in a greatly increased current is observed, and the corresponding voltage is read. This method yields the sum of the anode and cathode potentials. A complete study of decomposition voltages requires determination to be carried out separately for each electrode. For this purpose one of the methods already described may be applied. We shall confine ourselves to a consideration of cathodic results obtained by means of Nernst's technique of a large non-polarizable and a small working cathode as developed by Heyrovský since 1923 in the form of the mercury-dropping electrode already referred to on p. 103.

The Heyrovský Polarographic Method.

The Heyrovský method was made automatic by Heyrovský and Shikita (*Rec. trav. chim.*, 1925, **44**, 496) by means of the **Polarograph**. This instrument is shown diagrammatically in fig. 1. A steady current flows through the wire B, which is wound on a drum. This is revolved steadily by the clock M, the polarizing potential being thus increased automatically, while the current is registered photographically on the coupled revolving drum S. The value of the impressed P.D. is also registered automatically in steps of 100 m.v., and from it the P.D. between the dropping electrode and a standard calomel electrode can be derived. The figure also shows diagrammatically the galvanometer G with its lamp L and the dropping electrode vessel RVE. The sensitivity of the galvanometer is made variable by means of a shunt. Before starting an experiment dissolved oxygen is removed from the electrolyte by bubbling hydrogen through it for two or three hours.

To illustrate the application of the method we refer to fig. 2. In this the abscissæ represent the impressed P.D.s corrected to refer to a normal calomel electrode as standard, and the ordinates galvanometer readings. The two bottom curves are the polarograms of N/10 and N/1 sodium chloride solutions respectively. It will be seen that as the dropping electrode

potential is made more negative the current increases very slightly until a potential in the neighbourhood of 1·9 volt is attained. A very large increase of current there takes place, leading to a sudden change of direction in the polarogram curve. We may refer to this as a " bend ". It is sometimes

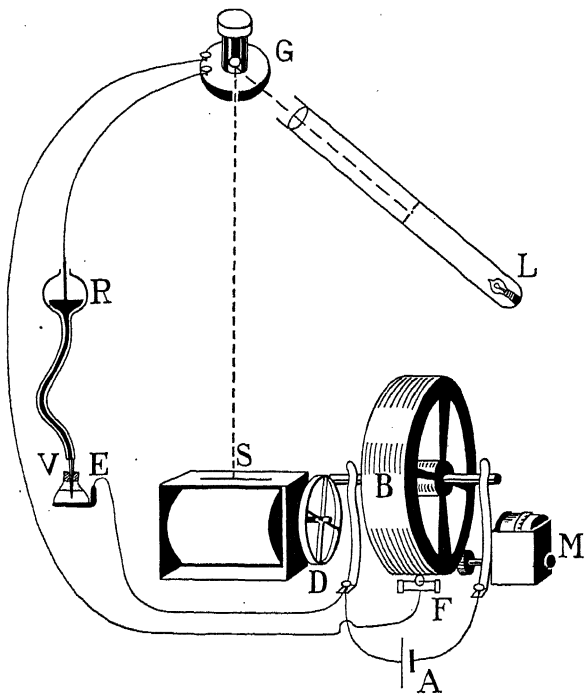


Fig. 1

described as an inflexion and sometimes as a break (German: Knick). The bend is due to the fact that sodium begins to deposit, forming a dilute amalgam in the cathode. As the bend-point Heyrovský takes the one where the curve shows a tangential slope of 45°, and it will be seen that the bend-point of the N/10 NaCl curve is about 0·06 volt more negative than that of the N/1 curve. This agrees with the fact that the

equilibrium potential of a sodium amalgam electrode of given concentration at laboratory temperature is more negative to a tenth normal solution of sodium ions than to a normal one by 0·058 volt. The top curve shows the effect of adding to a normal solution of NaCl, lead ions of 10^{-4} normal concentration. It will be seen that at an electrode potential of about —0·4 volt a large increase of current takes place due to the deposition of lead in the mercury cathode. On making the electrode potential more negative the current again as-

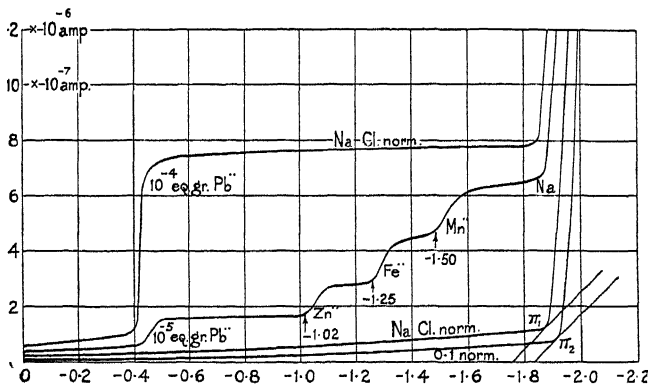


Fig. 2

sumes an almost constant value until the sodium bend occurs at the same electrode potential which was observed when pure sodium chloride was examined. The flattening of the polarogram curve after the lead bend is due to the fact that the increasing current has reduced the concentration of the lead in the electrode layer to practically zero, after which the rate of lead deposition is simply the rate of diffusion of lead ions through the diffusion layer of the cathode, and the current remains almost constant. The difference in galvanometer reading between the bend and the flattening-out points is a measure of concentration of the lead ions and is called by Heyrovský the " height of the lead wave ". Polarogram curves

are not smooth, as they appear in the diagram, but serrated owing to the continuous renewal of the mercury drops. The second polarogram in the diagram was obtained when lead, zinc, iron and manganese were added to the normal sodium chloride solution. The lead concentration is one-tenth of that in the top polarogram, and in agreement with this the position of the bend is about 0·03 volt more negative. It will also be seen that the height of the lead wave is about one-tenth of that in the top curve. The presence of the zinc, iron and manganese ions is clearly apparent in the polarogram.

The method is applicable not only to the detection of metal ions, but also to that of other reducible substances. In many cases suitable catalysts are added to facilitate reduction. When the dropping electrode is made the anode, it can be employed to detect anions which form sparingly soluble or complex salts with mercury. Heyrovský recommends his method particularly for the detection and approximate estimation of traces, and compares it with the spectrographic method in sensitiveness and economy in material. It has been applied successfully for examining reagents for traces of impurities, and for testing water for dissolved gases and other solutes. It has also been used in the sugar, fermentation, ceramic and other industries, and in biochemical research. For further information the reader is referred to numerous papers by Heyrovksý and his collaborators in the *Collection of Czechoslovak Chemical Communications*, to a pamphlet issued by the makers of the polarograph, Drs. V. and J. Nejdedlý of Prague, to the following reviews: J. Heyrovský, *Bull. Soc. chim.*, 1927, **41**, 1224, and W. Kemula, *Z. Elektrochem.*, 1931, **37**, 779), and to the following books: W. Böttger, *Physikalische Methoden der analytischen Chemie*, Teil 2, Leipzig, 1936, in which there is a section on polarographic methods by Heyrovský; and H. Holn, *Chemische Analysen mit dem Polarographen*, Berlin, 1937.

Residual Current. Polarization Capacity.

We have now to consider a matter first investigated by Helmholtz, viz. what happens when a P.D. is applied to a

cell, which is insufficient to cause the discharge of the ions known to be present. It might be thought that no current whatever would pass under such circumstances. This is, however, not found to be the case. A " residual " current is practically always observed, which may be large or small. We consider in the meantime the solution of an acid, in which a cathode is placed, that is kept less negative to the electrolyte than the equilibrium potential hydrogen/hydrogen ions. The electrolyte will ordinarily contain some oxidizing substance in solution, which may be oxygen from the air, or oxygen which has diffused from the anode. Oxidizing compounds, such as persulphuric acid, or hydrogen peroxide may also have been formed at the anode. These substances are slowly reduced at the cathode at a very much less negative potential than the equilibrium potential referred to above, and it is they that account for residual currents. Such currents will obviously be greatly promoted by vigorous stirring of the electrolyte, which brings the anode liquid rapidly to the cathode. Thus in rapid electrolytic analysis very considerable residual currents are frequently observed after all the ions corresponding to a given applied cathode potential have been removed, and they tend to mask the removal of definite ionic species. These residual currents can be very usefully diminished by the employment of reducing agents such as hydrazine or hydroxylamine salts. In solutions containing iron salts very large residual currents may arise. These are due to the oxidation of ferrous to ferric ion at the anode, and the opposing reduction at the cathode. This process may make the complete removal of metals such as copper from a solution containing large quantities of iron salts very difficult. The remedy—short of the employment of a diaphragm—is to use reducing agents, and to slow down the circulation of the electrolyte.

Residual currents may be removed by prolonged boiling of the electrolyte, and separating the electrodes so completely that no diffusion from one to the other is practically possible. Even so, when a potential difference, insufficient to cause discharge of ions, is first applied, a certain amount of current

will be found to flow. A transfer of electricity across the boundary electrolyte-electrode can, according to assumption, not take place. However, electrons will pass through the connecting wire to the cathode, where they remain, while positive ions move through the solution, taking up a position opposite them within molecular distance. Thus a " double layer " is built up in a similar way to that in which a condenser is charged, the union of the two charges being prevented, in the case of the electrode by insufficiency of applied potential for discharge of the ions, in the case of an ordinary macroscopic condenser by the dielectric. We may thus speak of the polarization capacity of an electrode. From experiments carried out by Bowden and Rideal (*Proc. Roy. Soc.*, 1928, A, **120**, 74) the writer calculated that this polarization capacity in the case of hydrogen ions amounts to 6 microfarads per square centimetre (*Trans. Faraday Soc.*, 1930, **26**, 22).

Where we are dealing with metal deposition, a certain very small amount of the metal, less than a unimolecular layer, may be deposited on an indifferent cathode at a lower potential than the discharge potential. This phenomenon was observed by Overbeck in 1887 (*Ann. Physik.*, 1887, **31**, 336), and may be compared with alloy formation.

The Nature and Structure of Electrolytic Metal Deposits.

Electrolytic metal deposits vary widely in appearance according to the conditions of their formation, and are variously described as adherent, loose, coarse-grained, fine-grained, bright, powdery, or spongy. In some cases they are found not to consist of the pure metal. The fact has already been referred to that electro-deposited iron and nickel frequently contain hydrogen. Nickel deposits formed in chloride baths sometimes contain chlorine. The absorption of elements like chlorine is particularly striking and has been much studied in the case of antimony, which forms so-called explosive antimony when deposited in the cold from antimonious chloride solutions containing an excess of hydrogen chloride.

It is probable that the presence of chlorine is due to the discharge of complex cations such as $NiCl^{+}$ and $SbCl^{++}$. According to a suggestion by Jordis (*Zeit. Elektrochem.*, 1905, **11**, 787) the chlorine may be present in an allotropic unstable metallic modification, which would account for the transformation on scratching, &c., of explosive antimony into the ordinary metal and clouds of antimonious chloride. Colloidal substances, or generally substances dispersed in the electrolyte in a state of fine division, may be co-precipitated to form part of the cathodic deposit. For such deposition to take place, it is necessary, according to experiments by Müller and Bahntje (*Zeit. Elektrochem.*, 1906, **12**, 317), that the particles should bear a positive charge.

Examination has shown that electrolytic metal deposits are in almost all cases crystalline. Such crystalline form may in the first instance have arisen from a primary amorphous mass, but when once present, crystals tend to grow as such. The nature of the metal deposit will depend greatly on the ease with which fresh crystal nuclei can be formed, the larger the number of nuclei, the more fine-grained the deposit; similarly, causes which hinder the growth of existing crystals promote a fine-grained deposit. It is probably due to the latter fact that colloidal substances have a profound effect on the structure of electro-deposits, making them very much more fine-grained, and in some cases giving them a bright burnished appearance. Such results are circumscribed by fairly narrow conditions of concentration and nature of colloid, a too high concentration inducing the formation of a powdery deposit. It is a general rule that the more complex the solution the more fine grained the metal obtained from it. Thus the complex cyanides of silver and copper yield very much more fine-grained deposits than, say, the simple nitrates. Whether this result is due to traces of colloidal substances, which may be so deposited from the complex ions, or whether it is due to purely electrical causes, connected with the very much more negative equilibrium potential in the presence of the complex ions, it is probably not possible to state. It is often found that metals deposited from solutions that might

be expected to liberate traces of colloidal hydroxide appear in a very fine-grained smooth state; but that whenever conditions arise in which recognizable quantities of hydroxide are precipitated, the metal assumes a powdery, spongy form. It is also conceivable that purely electrical conditions may make a negative cathode potential favour a fine-grained deposit. In this connexion the observation due to Coehn (*Zeit. Elektrochem.*, 1923, **29**, I) is of interest, that hydrogen bubbles liberated from an acid solution are large, and cling to the cathode. On the other hand, bubbles produced in alkaline solution remain quite small, and are repelled from the cathode. These observations were traced to purely electrical causes.

The initial structure of a metal deposit is of the greatest importance for its subsequent growth. Thus Kohleschütter proved that when silver is precipitated electrolytically from a double cyanide solution on a platinum electrode, and the electrode is then removed to a silver nitrate depositing bath, the silver crystals continue to grow, and the further deposit even after several hours has the appearance of one obtained from a cyanide, and not from a nitrate bath. (*Z. Elektrochem.*, 1913, **19**, 181). Blum and Rawdon (*Trans. Amer. Elektrochem. Soc.*, 1923, **44**, 397) showed that when copper is deposited from a sulphate solution upon either cast or rolled copper, which has been etched with nitric acid, the deposited metal consists of crystals, which are extensions of those in the metal base.

Effect of the Evolution of Hydrogen.

The evolution of hydrogen is a matter which may affect metal deposition in several ways. There is the possibility of absorption either physically or chemically, and this accounts for the very hard hydrogen alloys of iron and nickel already referred to. In many cases transient combination between metal and hydrogen may take place, the hydrogen subsequently leaving the metal in a roughened or powdery condition. Thus smooth platinum cathodes are roughened in course of time by the evolution of hydrogen. Copper and

bismuth are deposited in a powdery condition from dilute acid solutions from which hydrogen is being evolved.

Hydrogen evolution exerts another important effect, in decreasing the hydrogen ion, or increasing the hydroxyl ion concentration of the catholyte. In other words, hydrogen evolution always tends to increase the p_H of the cathode layer. Where vigorous circulation of the electrolyte takes place changes of acidity at the anode and cathode may neutralize each other; thus, if hydrogen is evolved at the cathode, and an equivalent amount of oxygen at the anode, the net result is only the removal of a small quantity of water with negligible effect on the acidity of the liquid as a whole. Where, however, stirring of the electrolyte is not so vigorous, it becomes necessary in the study of metal deposition to concentrate attention on the changes taking place in the catholyte alone.

We consider first solutions of low p_H. If these contain strong acid, then current is carried largely by hydrogen ions which partially replace those that are discharged at the cathode, and the p_H goes up only slowly during electrolysis. In the solution of a feeble acid from which hydrogen is being liberated, the hydrogen ions that have been removed are replaced also from the store of undissociated molecules. Secondly, we have to consider solutions of p_H corresponding to neutrality or alkalinity. In these the only reservoir of hydrogen ions is to be found in the molecules of water. We may take, for example, solutions of salts such as $MgSO_4$ or Na_2SO_4, or of alkalies such as NaOH. Our considerations will also apply to some extent to solutions of salts such as $ZnSO_4$ or $NiSO_4$ from which hydrogen evolution may occur concurrently with metal deposition. Returning to the instance of a sodium sulphate solution, it was at one time customary to consider that during electrolysis sodium ions were primarily discharged at the cathode with the formation of metallic sodium and that this subsequently acted on the water producing sodium hydroxide and hydrogen. According to present day theory this would simply amount to the successive discharging and recharging of sodium ions, and there is

no occasion to adopt such a view. In the case of neutral Na_2SO_4 we are considering, for example, it is important to distinguish clearly between the passage of the current through the electrolyte itself and the passage from the electrolyte to the electrode. During the former the share taken by the hydrogen ions of the water is vanishingly small. When, however, it comes to the passage of the current from the electrolyte to the electrode the work required to discharge sodium ions is so much greater than that needed for hydrogen ions, that we must assume the latter to be discharged directly in spite of their small concentration. The hydrogen ions which disappear are replaced at once by fresh ones provided by the water molecules, and thus hydroxyl ions appear whenever hydrogen ions are removed. The charges of the new hydroxyl ions are balanced or neutralized, partly by the departure due to ionic migration of other anions and partly by the arrival of fresh cations. According to the nature of the cations present the production of hydroxyl ions may or may not lead to the precipitation of hydroxides or of basic salts. In a neutral solution of Na_2SO_4 a rapid increase of hydroxyl ion concentration and of p_H thus takes place from neutrality to appreciably alkaline values. In a solution of an alkali such as sodium hydroxide the absolute rise of $[OH^-]$ is equally great, but as the initial $[OH^-]$ is already great, the relative rise and hence the increase in p_H will be small.

In order to inhibit a rapid rise in p_H at the cathode in solutions that are nearly neutral, buffering mixtures such as sodium acetate plus acetic acid may be added. In such circumstances hydroxyl ions are removed through the agency of molecules of undissociated acid with the production of water and the anion—in the present case acetic ion. In some applications of metal deposition such as electro-plating it is probable that the best p_H value is one at which a trace of colloidal hydroxide or basic salt is precipitated with the metal. When, however, this p_H value is exceeded, easily recognizable quantities of metal hydroxide are precipitated which make the deposit spongy and useless.

Throwing Power and Excessive Crystal Development.

With certain electrolytes, the metal deposit is found only on those parts of the cathode which are nearest the anode, with others it appears capable of spreading over the whole of the electrode, even to recesses and other difficultly accessible parts. The latter class of electrolytes are said to have good " throwing power ", a property which is of great value, e.g. to the electro-plater. Electrolytes with poor throwing power are those containing simple ions, and generally those that show slight polarization and metal overvoltage. On the other hand, electrolytes with good throwing power are solutions of complex salts, also those containing colloids, and generally such as exhibit a high degree of metal overvoltage. The connexion between metal overvoltage and throwing power is purely electrical, and not difficult to understand. The metal cathode may be considered to be at practically uniform potential; when, however, metal overvoltage makes it highly negative to the liquid in its immediate vicinity, the latter will be positive to the cathode in more inaccessible parts, and hence the spreading of the current to these. A contributory factor to good throwing power is good conductivity of the electrolyte, since this will assist the current to reach the parts of the cathode most distant from the anode. Generally speaking, good throwing power and a fine-grained deposit go hand in hand.

The reverse of good throwing power is exhibited by those metals that show a great tendency to crystal growth. As already stated, they are in particular soft metals, such as silver, tin and lead, when deposited from solutions of their simple salts. They form deposits which are useless both for purposes of electrolytic analysis and of electro-plating. The phenomenon of coarse crystal formation can be observed particularly well in the formation of the familiar lead and tin trees, which are obtained by placing zinc rods in the appropriate lead and tin solutions. The growth of these trees is an electrolytic phenomenon, and is so rapid that the electrolyte in contact with the crystals soon becomes almost exhausted

of metal ions. The branches therefore seek the more concentrated solution, thus growing to considerable distances from the zinc rod. The growth of the tree may be hindered by revolving the rod rapidly, and thus opposing changes of concentration in the electrolyte.

In conclusion, we consider the effect of agitation of the liquid, of current density, of concentration of the electrolyte, and of temperature on electrolytic metal deposits. Except in extreme cases the electrode layer does not slip on the electrode during agitation of the liquid, and the effect of stirring is therefore only indirect in maintaining the composition of the electrolyte in the electrode layer at nearly the same value as in the bulk of the solution. We realize, however, the extreme importance of this function, when we remember the great changes that may take place in the composition of the electrode layer, if the electrolyte outside it is not renewed either mechanically or by other means. Whenever a separation of consecutive electrolytic processes is required, it is imperative that there should be circulation of the liquid. The greater this is, the higher is the permissible current density, and the shorter the time necessary for the completion of a given electrolytic process. In an experiment by the writer it was thus shown that in an acid dilute solution of copper sulphate, and in the absence of artificial stirring, a given current was employed to the extent of 60 per cent in liberating hydrogen. When, however, vigorous stirring was resorted to under otherwise identical conditions, the evolution of hydrogen was suppressed entirely.

Increase of current density increases the rapidity with which changes of concentration in the electrode layer take place, and is counteracted by increase of average concentration in the electrolyte, and particularly by increased stirring. Apart from this, a high current density is believed to induce the formation of crystal nuclei, and thus to render metal deposits fine grained. High concentration is believed to have a similar effect. Rise in temperature, as we have already seen, always reduces metal overvoltage, and thus promotes crystal growth. As a result, it tends to render

deposits coarse grained, and it will diminish throwing power. On the other hand, it may be taken that it generally improves the adherence of metal deposits, so that in many cases a high temperature is advantageous for purposes of electrolytic analysis.

ADDENDA

Note on Mobilities and Velocities of Ions.—The constants l and u, as defined in Chapter II, are of fundamental interest. As has been explained, their evaluation assumes that determinations have been carried out on completely ionized solutions. The symbols therefore refer to solutions of zero concentration, and when necessary the subscript 0 should be attached to them. Thus equations (14) of p. 21 become $l_{k0} = \Lambda_0 T_k$, $l_{a0} = \Lambda_0 T_a$, and equations (6) of p. 20 become $u_{k0} = l_{k0}/F$, &c. Many writers use the symbols l and u with a wider significance than we have attached to them in this treatise, defining them by the equations $l_k = \Lambda T_k$, $u_k = l_k/F$, &c., so that by equation (13), p. 21, we have $l_k = \alpha l_{k0}$, $u_k = \alpha u_{k0}$, &c. The quantities l and u are thus no longer independent of concentration. The ratios $l_k : l_a$ and therefore transport numbers remain independent of concentration on the basis of the older theory as propounded in Chapter II. Modern investigation has not verified this conclusion, and therefore proves in conformity with other results that the older Arrhenius theory is at best only a partial presentation of the facts.

Note on the Helmholtz Equation for a Galvanic Cell.—The deduction of the Helmholtz equation No. (10), as given in Chapter IV, restricts it in the first instance to changes taking place at constant volume, the cycle considered as well as the equations (5), (6) and (8) being based primarily on the assumption of constant volume. The heat of reaction therefore refers to constant volume, and in the partial differential quotient occurring in the equation volume is a constant. A review of the deduction in which the remarks made about the applicability of the Gibbs-Helmholtz cycle to changes taking

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